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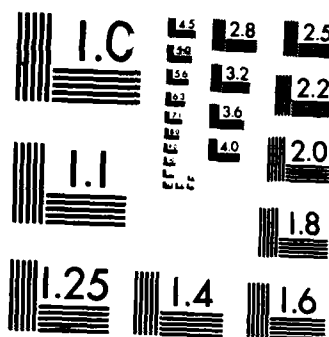
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AFWAL-TR-86-2030

AD-A174 128

CARBON SLURRY SECONDARY ATOMIZATION

J.R. Longanbach and A. Levy
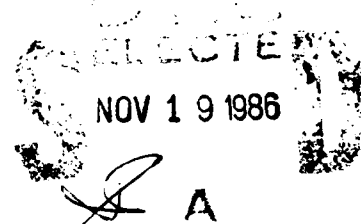Battelle Columbus Division
505 King Avenue
Columbus, Ohio   43201

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University of California
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September 1986

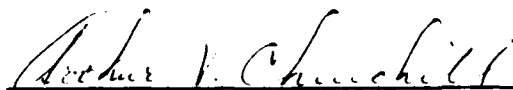OTIC FILE COPY

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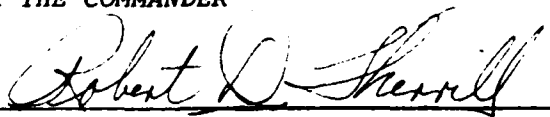
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AD-A174128

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY N/A	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-86-2030

6a NAME OF PERFORMING ORGANIZATION Battelle Memorial Institute Univ. of Calif. (Subcontractor)	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Aero Propulsion Laboratory (AFWAL/POSF)
6c. ADDRESS (City, State, and ZIP Code) 505 King Avenue, Columbus, Ohio 43216 Davis, California 95616		7b. ADDRESS (City, State, and ZIP Code) WPAFB, OH 45433-6563

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F33615-84-C-2410

| 8c. ADDRESS (City, State, and ZIP Code) | 10. SOURCE OF FUNDING NUMBERS |

	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
	62203F	3048	05	34

11 TITLE (Include Security Classification)

Carbon Slurry Secondary Atomization

12. PERSONAL AUTHOR(S)
J.R. Longanbach and A. Levy - Battelle/Chung K. Law - University of California

13a. TYPE OF REPORT Interim Report	13b. TIME COVERED FROM 8/84 TO 2/86	14. DATE OF REPORT (Year, Month, Day) 1986/September	15. PAGE COUNT 54

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Slurry Fuels, Carbon Slurry, Atomization, Microexplosions
21	04		
21	05		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)   were screened

The purpose of this work was to screen various agents that might be incorporated with the carbon and/or with the JP-10 phase of the slurry for their ability to cause micro-explosions in slurry droplets on heating (and to develop a method to observe and evaluate the behavior using laser radiation as the energy source for explosion initiation).

Experimental investigations have been conducted on effect of additives in inducing and intensifying microexplosion of combusting carbon slurry droplets. A new droplet generator capable of producing small droplets of well controlled size was developed for the slurry fuel used. Agglomerate fragments produced through microexplosion were collected by using an impactor-type sampling probe and statistically analyzed. Results show that the fragment sizes follow the log-normal distribution, and that addition of 5 percent volatile miscible fuels to the carbon slurry can significantly reduce the mean fragment size.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL Eva M. Conley	22b TELEPHONE (Include Area Code) (513)255-7211 — 22c. OFFICE SYMBOL POSF

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

☆U.S. Government Printing Office: 1988—507-047

SUMMARY

This is a two-part program on ways to achieve secondary atomization of JP-10/carbon slurry jet fuels. Various agents that might be incorporated with the carbon and/or with the JP-10 phase of the slurry were screened for their ability to cause microexplosions in slurry droplets on heating and a method to observe and evaluate the behavior using laser radiation as the energy source for explosion initiation was developed.

Experimental investigations were also conducted on the effect of volatile additives in inducing and intensifying microexplosion of combusting carbon slurry droplets. A new droplet generator capable of producing small droplets of well-controlled size was developed for the slurry fuel used. Agglomerate fragments produced through microexplosion were collected by using an impactor-type sampling probe and statistically analyzed. Results show that the fragment sizes follow log-normal distribution, and that addition of 5 percent volatile miscible fuels to the carbon slurry can significantly reduce the mean fragment size.

FOREWORD

This report describes two programs conducted under this task. One program was done under the direction of A. Levy at Battelle Columbus Division, and the second program was conducted by Professor C. K. Law at the University of California, Davis.

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SCHOLARLY RESEARCH PROGRAM
Carbon Slurry Secondary Atomization

by

J. R. Longanbach, A. Levy and Chung K. Law

I. INTRODUCTION

As a means of improving the range and payload of cruise missiles,
the Air Force is developing fuels with high-volumetric energy content. To
increase the energy content of these fuels from their current peak level of
about 160,000 Btu/gal to a desired 180,000 Btu/gal, the Air Force has developed
a series of solid-carbon slurry fuels using JP-10. A 180,000-Btu/gal carbon
slurry-jet fuel requires approximately 63-weight-percent carbon load.

Ultimately a successful slurry fuel must possess 5-year storage
stability, fluidity down to -65 F, high Btu/gal heat of combustion, and a
combustion efficiency greater than 99 percent. Several reasonably stable,
low-viscosity carbon slurry-fuels have been developed. A critical problem at
the moment is combustion efficiency. Burnout of carbon in a slurry lags the
vaporization and burnout of the JP-10. This results in unburnt carbon in the
exhaust with resultant combustion efficiencies of 95 percent or less. We well
recognized from past work with these slurry jet fuels, and from work with
coal-water mixtures, that agglomeration of carbon particles in the former
instance and coal particles in the latter occurs. To improve the efficiency
the size of slurry droplets emanating from the fuel nozzle must be decreased.
This required improved atomization. One solution is secondary atomization of
the primary slurry droplet. This program is directed to this topic of secondary
atomization of carbon slurry-jet fuels.

Two methods have been studied to induce secondary atomization. In
the studies by Professor Law, volatile additives have been incorporated within
the droplet. For suitable components and composition, rapid gasification
within the droplet interior can occur spontaneously, leading to intense
internal pressure build-up and consequently catastrophic fragmentation of the
droplet. The primary objective has been to explore the efficiencies of
various additives in inducing and intensifying droplet microexplosion.

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Two companion experiments have also been conducted, respectively, involving determining the liquid temperature at the state of gasification, and measuring the fragment statistics due to microexplosion of freely-falling droplets.

In the studies by Battelle, explosive compounds were added to carbon-slurry jet fuel droplets and attempts were made to detonate them either by rapidly increasing the temperature with energy input from a continuous laser, or by inducing a shock wave in the sample by energy input from a pulsed laser.

II. BACKGROUND

1. General

The subject of secondary atomization relates to the combustion of two types of carbon fuels today, which are similar in some ways and possibly dissimilar in other ways. The two slurry fuels are carbon slurry jet fuel and coal-oil-water fuels for utilization in furnaces and boilers. The carbon slurry jet fuel is typified by a highly refined carbon, at a concentration of 55-65 percent, and ground to 1-5 μm, in a highly refined fuel such as JP-10. The coal slurry fuel may be 60-70 percent coal in an oil (possibly a No. 6 oil) and more recently in water. The coal particles are usually ground to 70 percent -200 mesh ($<$74 μm).

In either instance, the carbon slurry fuel is atomized as a spray; the fuel droplets then penetrate into the combustion interior, react with hot oxidizing air, and so undergo vaporization and combustion. Combustion of the JP-10 portion of the fuel spray is a vapor phase reaction. As a consequence, as the JP-10 is volatized and consumed, the carbon particles are further concentrated in the droplet and tend to agglomerate. This results in longer combustion times and in some inefficiency, as some particles go through unburned. The problem may be further exacerbated for carbon slurry jet fuels since the more refined the carbon, often the less hydrogen attached to it, making it more difficult to burn the carbon particles.

One possible solution to the carbon particle agglomeration problem is to promote secondary atomization processes, i.e., add an ingredient to the fuel to essentially explode the fuel droplet into smaller droplets. The overall effectiveness of this procedure has been demonstrated for many

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years. Three earlier references to this procedure are those of several Russian investigators who showed that residual oils burned cleaner upon emulsifying the fuel oil with water so that the entrained water exploded to help disperse and open up the cenospheres for better combustion.[1,2,3]

In more recent times, C. K. Law, F. L. Dryer, and others have examined secondary atomization in more depth. In considering secondary atomization, reference is made to three types of processes: disruptive combustion, microexplosion, and scattering. The differences in these three processes may be more semantic than real.

C. K. Law analyzes the combustion of coal slurries by considering quiescent combustion and disruptive combustion.[4] In quiescent combustion. Law presents a system in which mixing in the droplet is rapid. Internal circulation is of sufficient intensity that temperature and concentrations are uniform. This leads to more volatile components being preferentially removed, leaving behind a droplet with less volatiles and a higher concentration of coal. This leads to agglomeration. As Law points out, a 100-μm droplet containing 1 percent coal will yield a 20-μm agglomerate. This agglomerate size becomes essentially independent of initial particle size.

If internal circulation is mild, diffusion rather than convection becomes the dominant mode of transport within the droplet. To illustrate this effect, Law considers a droplet of two miscible liquids with vastly different volatilities. In this system, if the heat diffusion rate is a couple of orders of magnitude faster than the mass diffusion rate, i.e., the Lewis number is significantly >1, say 5-10, then one begins to superheat the low boiling point liquid in the center of the droplet, and the result is an explosion of the droplet, i.e., secondary atomization, producing many smaller droplets.

Yap, Kennedy, and Dryer have recently discussed this same topic and the attempts to distinguish between disruptive burning and microexplosion[5]. In discussing the proposition of a "toroidal vortex model", as a more accurate description of the liquid phase for analyzing the behavior of water in hexadecane emulsion systems, Yap et al. state "the term 'disruptive' burning is reserved for describing the internal vaporization within multi-component solution droplets, whereas the term 'micro-explosive' combustion refers to the much more rapid internal vaporization of water droplets occurring within emulsified fuel drops." Using these definitions, the nature of the multicomponent fuel must be questioned. Lasheras et al. state "for disruptive

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burning to occur, not only a minimum difference between magnitude of the boiling points of the component must exist, but the relative quantitites of the components must fall within a certain range dependent on the mixture constituents".[6] It may follow from this that a two-component, solid-liquid slurry cannot be analyzed in the same manner as a multicomponent solid two-liquid slurry--a point that may bear closer scrutiny relative to the experiments being reported.

2. Microexplosions in Miscible Mixtures

Several investigators have observed that solvent refined coal (SRC) burns "disruptively." Kramlich, Seeker and Payne identified at least two sources for this behavior.[7] When SRCII heavy distillate is mixed with heptane, the heptane boils as the fuel mixture droplets heat up, breaking up the fuel droplet to produce a new set of smaller droplets. This process is called secondary atomization. Thus, SRC produces soot particles, as do the unblended fuels, and the soot particles terminate in microexplosions.

The second explosive process generally occurs in one or two directions only, is violent enough to disperse the entire particle, and occurs in every particle. Called droplet dispersion, Kramlich, Seeker, and Payne found that this reaction occurred for each fuel type studied, with the exception of pure heptane which terminated by evaporization, and an Indonesian/Malasian crude which contained a very high asphaltene concentration and terminated by censophere formation. The mechanism of droplet dispersion may include coking to produce volatiles which then boil to produce a microexplosion of the solid particles.

In an early study of secondary atomization in hydrocarbon blends, Lasheras, Fernandez-Pello and Dryer showed that vaporization-disruption can occur only when (1) a thermal transfer is faster than mass transfer (high Lewis number) so that the internal volume of the particle will heat more rapidly than diffusion-evaporation can occur, and (2) one component has a higher boiling point than the superheat limit of the lower boiling component, so that a liquid phase will exist to hold the bubble together during heating.[6] This means that secondary atomization can be induced or suppressed by controlling the composition and boiling point ranges of the components in a mixture and the external pressure in the system. The presence of a filament to suspend the

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drop, as has been practiced in some experimental studies, alters the nucleation and heat transfer processes. The net effect is to increase the intensity of secondary atomization.

Gallahalli showed that in freely falling drops the time to disruption, which should be short if a large amount of the drop mass is to be dispersed, is increased by increasing the drop size and the fraction of the volatile phase. Methanol-oil drops were shown to burst more vigorously and rapidly than water-oil drops.[8]

A theory and model which describe secondary atomization processes in two-component mixtures have been developed by Law.[9] In a subsequent review Law also predicted that the secondary atomization effect would be increased at higher pressure because the boiling temperature of the volatile phase would be raised, but the limits of superheat would be affected only slightly.[10] This was subsequently confirmed for both miscible, multicomponent mixtures and water/oil emulsion droplets.[11] A final observation on miscible multicomponent mixture microexplosions is the visual observation, reported by Law, of two nucleation bubbles in a single droplet. The location of these bubbles in the droplet shows that homogeneous nucleation of volatilization occurs on a spherical surface within the particle where the superheat conditions are favorable, rather than in the center of the droplet.[12]

3. Microexplosions in Non-Miscible Mixtures

Law et al, have extended their multicomponent studies to coal/oil and coal/oil water mixtures.[13] The combustion characteristics of coal/oil mixtures are dependent on the internal mixing in the droplets. At the rapid-mixing limit, the volatile components are able to get to the surface and evaporate, so that batch distillation occurs and the non-volatile coal particles agglomerate. Agglomeration can be significant even at low coal loadings. A 100-μm droplet containing 1 percent coal particles will produce 20-μm agglomerate.[13] When internal circulation is weak, diffusion is rate limiting. The coal particles can serve as nucleation sites for internal boiling. Fragmentation of the droplet occurs and can occur again when the smaller droplets are formed by secondary atomization. To obtain these conditions the droplet should be small, the oil should be viscous and should contain high and low boiling components.

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The addition of a small amount of water can be used as an alternative method to induce secondary atomization. Initiation of water boiling is insensitive to internal motion and fuel composition. Since small amounts of water are normally present in coal, no special effort may be necessary to introduce water. The presence of 5 percent water in a coal/oil/water emulsion stabilizes the emulsion and causes early anad violent secondary atomization. The coal particles do not have to be ground fine. Particle burning time is not dependent on initial particle size.

Studies of the coal/oil mixtures suspended from fine wires in a heated atmosphere suggest that the addition of methanol would be useful to shorten the ignition delay time and that the addition of water might effectively initiate secondary atomization by microexplosion, which leads to shortening of the overall combustion time.[14]

Combustion of coal/methanol slurries (CMS) has also been studied. There is some interest in these slurries because of the low freezing point of methanol which would allow transportation of the slurries through a pipeline in a cold climate. Emissions of NO_x and SO_x would also be decreased by burning CMS. Studies testing droplets suspended on a wire, or in a platinum basket in a hot atmosphere, show that combustion occurs in two stages. The coal volatile matter and methanol burn in the first stage, scattering the coal particles in the process. This scattering is different from secondary atomization. The particles then burn rapidly because they are finely dispersed. During particle burning no disruptive burning was observed.[15]

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III. EXPLOSIVE ADDITIVE STUDIES

1. Results

1.1 Previous Work

The use of explosives incorporated in a carbon-slurry fuel to enhance atomization has also been studied, although much less extensively than the use of volatile additives. All of the normally obtainable and suitable "explosives" are chemically stable at ambient conditions. Obtaining an explosion rather than mere burning of a chemically stable compound can be a complex and difficult task requiring the achievement of a very specific set of reaction conditions.

Early studies of the explosive behavior of methyl nitrate vapor in the presence of oxygen and an inert gas in a heated tube illustrate some of the problems.[16] Normally, an exothermic reaction must self heat to a temperature above the surroundings to accelerate the chemical change. Loss of heat to convection and conduction opposes the process. Therefore, dilution with inert gases might be expected to quench ignition. But in the case of methyl nitrate, the presence of nitrogen or argon in all concentrations increases the tendency to explode because self heating is of secondary importance. The explosion develops by a chainbranching mechanism and diffusion to the walls, which is inhibited by the presence of an inert gas, is the principal quenching mechanism. The half-life for thermal decomposition of methyl nitrate varies from 5 seconds at 275 C to 2 ms at 425 C. Above 300 C all of the methyl nitrate decomposes during the induction period and the explosion occurs in a mixture of nitrogen dioxide, methyl alcohol and formaldehyde.

At least one instance of "chemically enhanced" combustion of a water slurry-fuel has been published. In a recent patent, Olen suggests the use of 100 to 5000 ppm of a water soluble explosive taken from picric acid, alkali picrates and heavy metal picrates, guanidine and nitroguanidine in a 65 to 80 percent coal/20-35 percent water composition to detonate early in the combustion process, producing a secondary dispersion of fuel particles.[17] Unfortunately, this patent does not appear to have been experimentally verified.

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There is a large amount of literature on explosives, which have been a subject of active study in many nations since black powder was introduced in Europe around 1250 A.D. Explosives are characterized by rapid reaction times, generally 10^{-6} seconds and the production of large volumes of gas. The rate is controlled by shock transfer and initiation occurs either by temperature or shock with an activation energy of typically 30 to 60 kcal/mole. The shock wave intensity depends on confinement, density of materials and geometry.

Explosive types include primary, secondary, high explosive and propellant in order of decreasing sensitivity to energy input. Only a few ingredients are used because of safety and cost. Accessibility further limits the number of explosives available for a study such as this one.

1.2 Laser Ignition

Heat to cause ignition can be introduced by convection and/or radiation. In the present program it was decided to use laser ignition. Light from all lasers is highly monochromatic and coherent; the beam is perfectly parallel, easily controlled and directed using shutters, lenses and mirrors.

Realization of the potential of using lasers to induce heating/pyrolysis in solids,[18,19] to ignite fuel gases [20] or droplets and to initiate deterioration [21] date to 1967-1968. Lasers have a number of advantages in attempting to achieve point ignition. Energy release can occur in a very short time, or in a very small area, and the quantity of energy can be measured accurately.[22]

Early experiments on the pyrolysis of finely divided coal using a 15-kw continuous CO_2 laser (10.6μm) showed that the heating processes in the particles can be decoupled from secondary reactions which occur due to the presence of a hot gaseous atmosphere. The use of laser heating also eliminates the need for a hot wall structure and allows better control of the time-temperature profile and gaseous atmosphere present at the particle surface.[23] Heating rates of 10^5 K/s and temperatures of 1300-1800 K can be achieved, which simulates pulverized fuel combustion or entrained flow gasification conditions. However, with small particles heat loss is rapid

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and the heating behavior of the particle follows roughly the heat input from the laser beam.

Using more complex experimental arrangements, it has been possible to irradiate free falling particles with a pulsed laser beam to obtain mass spectra of fragmented individual aerosol particles.[24] A Nd-YAG laser has been used to fragment organic or inorganic ions using a pulse of 2 J of energy in less than 100 μs. The use of a freely moving particle avoids substrate-particle interaction, including conductive heat loss.

Inducing detonation of a single substance or mixture can be difficult. For instance, the mechanism of breakdown in methane-air mixtures caused by the very rapid energy input from a laser has been found to be very complex. The point facing the beam absorbs the incoming energy which leads to the formation of an asymmetrical initiating source with energy in excess of that needed for ignition, and possibly capable of forming a blast wave which may be powerful enough to cause detonation.[25]

However, simply adding a large amount of energy to a small point on the surface of a carbon particle is not sufficient to insure combustion. In a study of laser-ignition of electrode carbon particles in a nitrogen-oxygen atmosphere, Ubhayaker and Williams showed that small carbon particles routinely extinguished without significant burning after laser ignition.[26] The surface oxidation reaction to produce CO has an Arrhenius activation energy of 18 kcal/mole and an order of 0.5-1.0. Variation in the oxygen fraction (0.5-1.0) and pressure (0.5-3 atm) showed that the burning rate is oxygen-diffusion controlled and, as the particle size (50-200 μm) decreases, the reaction rate becomes smaller than the diffusion rate, causing extinction. This occurs even though the surface temperature is raised to vaporization temperature (4500 K) via a 35 J pulsed ruby laser.

A study has been reported on the burning of dried agglomerates from carbon-slurry fuels.[27] Agglomerates having diameters of 750 μm were supported in the post-flame region of a flat flame burner. These studies predicted the lifetimes of carbon-black slurry drops in environments typical of combustion chambers. The work included several carbon-black formulations, initial drops sizes from 10-1000 μm, fuel equivalence ratios of 0.2-1.4 and temperatures of 800-1950 K at atmospheric pressure. The two-stage combustion process consisted of (1) heatup and gasification of the liquid fuel leaving

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the slurry particles in the drop as a porous agglomerate, and (2) the agglomerate reaction stage which lasts an order of magnitude longer and is the rate controlling step for complete combustion. Although the addition of lead was found to increase the agglomerate burning rate by as much as a factor of two, the study concluded that attention should be focussed on improving atomization of the agglomerates.[27]

1.3 Experimental Method

The experimental program consisted of obtaining a sample of carbon-slurry jet fuel from the U.S. Air Force and adding a variety of explosives to it. Small drops of the slurry were supported in several ways in the path of a laser and exposed to continuous radiation, using a CO_2 laser or a pulse of radiation from a Nd-YAG laser. Energy output was monitored by an infrared-sensitive diode in the case of the continuous laser and by a microcalorimeter when the pulsed laser was used. The experiments were also monitored visually.

Various agents that could be incorporated with the carbon and/or with the JP-10 phase of the slurry were screened for their ability to cause microexplosions in slurry droplets on heating. Solid organic nitrates, for instance RDX or TNT, were incorporated at low percentages into the slurry. Droplets, some suspended from quartz fibers, were exposed to laser radiation to initiate the microexplosion. The explosions or change in the droplets were observed visually and by recording temperature changes.

1.4 Carbon Slurry-Jet Fuel

A sample of carbon dispersion fuel was received from personnel at Wright-Patterson Air Force Base. The sample was produced at Sun Tech, Inc., Marcus Hook, PA. The sample had a stated flash point of 125 F and was labelled as follows:

SF-2 (783)

83-POSF-1275 McCoy.

A preliminary experiment showed that the fuel could be passed through a 0.25 mm quartz capillary using a disposable syringe as the driving force. This technique produces drops having a radius of about 819 μm which are within

the calculated size range which could be vaporized by the 90 W laser beam in less than 100 milliseconds, using the vaporization of water as a model for the heat requirement.

1.5 Explosives

Table 1 lists the properties of the explosives used in this study. They range from oxidizers to a possible primary explosive. Most are secondary explosives, available commercially because they are not very sensitive to impact, shock and elevated temperature. For instance, ammonium picrate has been used in armor-piercing gun projectiles because of its insensitivity to impact and shock.[28] TNT is relatively insensitive to impact, friction, shock and electrostatic energy. It has been fired in high-acceleration gun projectiles with reported premature rates of less than one in a million.[28]

The detonation temperature of tetryl is reported to be 2915 K[28] and the detonation pressure of TNT is 18.9 GPa (130,000,000 psi).[28]

Thus, it was not expected to be an easy task to detonate these explosives in a carbon slurry via laser radiation, either by rapid heatup or by generation of a shock wave.

1.6 Continuous-Laser Apparatus

A 90-W CW CO_2 laser was selected for use initially. A small (4 in. x 5 in.) box to house the droplet holder was constructed of Lucite. Lucite is opaque to the 10.6 μm CO_2 laser beam and allows the experiments to be monitored visually.

A diagram of the apparatus is shown in Figure 1. It consisted of a 1-inch diameter electronically-operated silver-alloy coated shutter (A.W. Vincent Assoc.) which could be opened for a time from 6 ms to infinity. The laser beam reflected to a firebrick when the shutter was closed. When opened, the beam passed through a germanium beam splitter (1-inch diameter x 2 mm) and was reflected by mirrors and focused on opposite sides of the sample through two 1-inch-diameter F4 lenses, and 19.05-mm-diameter windows, both made of BaF_2. The sample was held on the end of a stainless steel needle or quartz tube suspended from a 1-ml disposable syringe. The droplet could

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TABLE 1. PROPERTIES OF EXPLOSIVES

Name	Purity	Formula	Molecular Weight	Explosive Type	Supplier
Ammonium Nitrate	99.7%	$NH_4 NO_3$	80.	Oxidizer	"Baker Analyzed" Reagent
Picric Acid (2,4,6 trinitrophenol)	98%*	$C_6H_2(NO_2)_3OH$	229.	Secondary	Aldrich Chemical Co., Inc.
Ammonium Perchlorate	99.8%	NH_4ClO_4	117.5	Oxidizer	Aldrich Chemical Co., Inc.
Sodium Azide	99%	NaN_3	65.		Aldrich Chemical Co., Inc.
TNT (trinitrotoluene)		$C_6H_2(NO_2)_3CH_3$	227.	Secondary	
Tetryl (trinitrophenylmethylnitramine)		$C_6H_2(NO_2)_3 NCH_3NO_2$	287.	Secondary	Aldrich Chemical Co., Inc.
Nitromethane	96%	CH_3NO_2	64.	Secondary	Aldrich Chemical Co., Inc.
Tetranitromethane	98%	$C(NO_2)_4$	196.	Explosive	Aldrich Chemical Co., Inc.

*65% solids in water.

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DISPOSABLE SYRINGE CONTAINING SLURRY

IR DIODE TO DETECT HEAT IN DROP

OSCILLOSCOPE

SCREWS TO ADJUST POSITION OF DROP

DROPLET

1" DIA. BaF₂ WINDOWS IN BOX

1" DIA. F4 BaF₂ LENSES

LUCITE BOX

SET SCREW TO HOLD SYRINGE

MIRRORS

MIRRORS

GERMANIUM BEAM SPLITTER (1" DIA × 2 mm)

FIREBRICK LASER LIGHT HEAT SINK

1" DIA. SILVER ALLOY ELECTRICALLY OPERATED SHUTTER

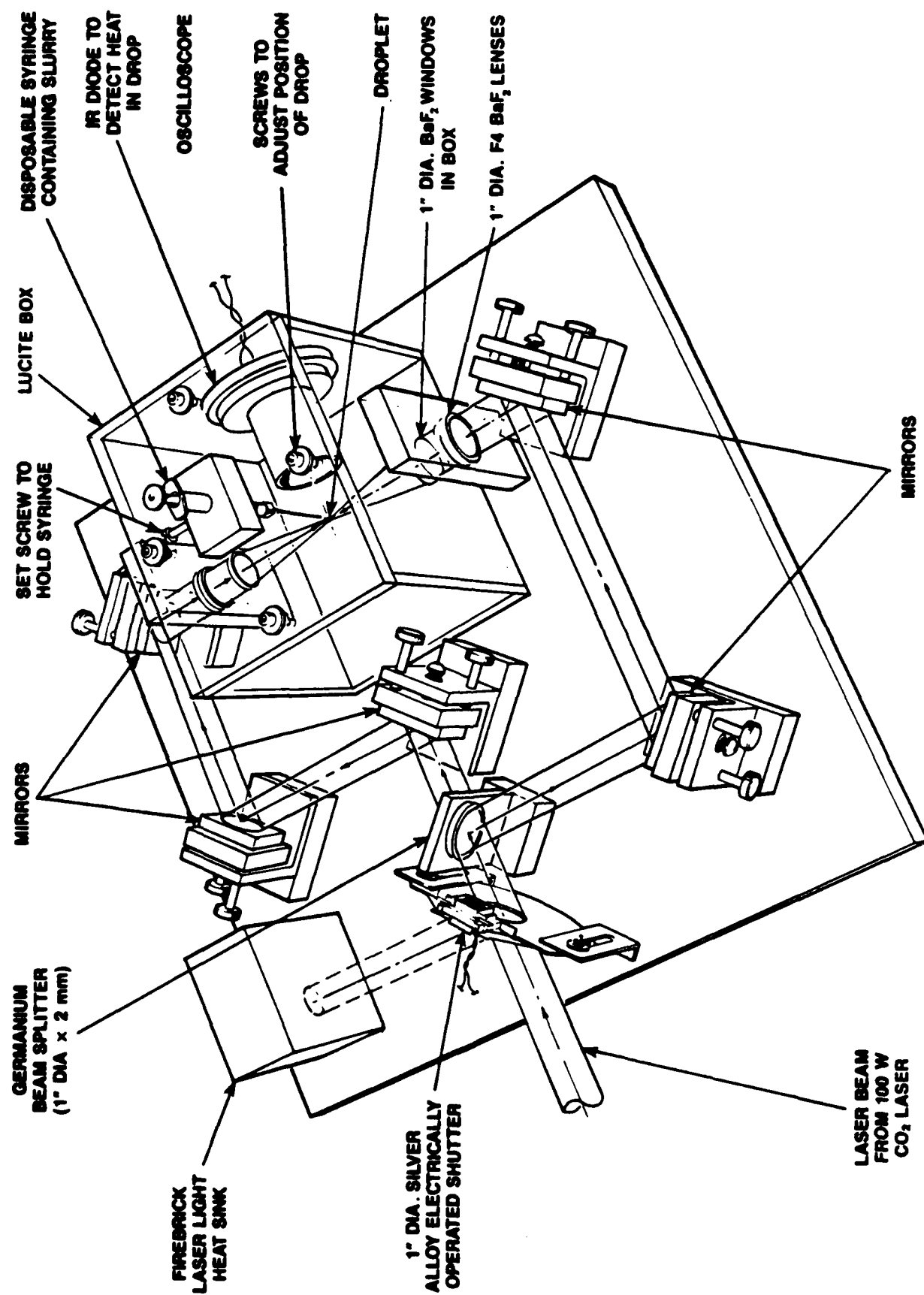LASER BEAM FROM 100 W CO₂ LASER

FIGURE 1. CONTINUOUS LASER APPARATUS

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be centered in the laser beam by various set screws on the syringe holder assembly.

The infrared light from heating of the sample drop was collected on a diode, placed normal to the direction of the laser beam and covered with a piece of acetate which would not pass reflected 10.6 µm laser radiation. The heat output to the diode was recorded on an oscilloscope and the trace was photographed with a Polaroid camera over a time-intensity grid to obtain a permanent record. The oscilloscope sweep was triggered by opening the shutter.

In later experiments, a Norland 2001A programmable oscilloscope was used to digitally collect and average multiple heat traces to measure averaged heat output versus time.

1.7 Pulsed-Laser Apparatus

A Nd-YAG (Neodymium-Yttrium Aluminum Garnet) pulsed laser which supplied one joule of energy at 1.06 µm in a single 25-nanosecond pulse was used. The focus was very narrow, 1 mm. A microcalorimeter was placed about 10 cm from the sample to measure the energy emitted by the explosion. A narrow band pass filter removed any reflected 1.06-µm radiation.

1.8 Carbon-Slurry Drop-Size Measurements

Tests with 0.25-mm- and 0.32-mm-ID fused silica tubing showed that the carbon slurry fuel sample could pass through the tubing. Average drop sizes formed were 820 and 1040 µm radius, respectively, based on the average weight of 10 drops from each tubing size, and a slurry bulk density of 1.24 g/ml at room temperature.

1.9 Initial Continuous-Wave Laser Tests

A number of problems had to be solved initially with the continuous wave laser and sample holder. The power of the CW CO_2 laser was measured at 50 W rather than the rated output of 90 W. The variation in power output over time seemed to be minor.

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The initial focus of the beam was very small. The laser beam seemed to "drill a hole" in the droplets. The focus was widened as much as possible without significant changes in the apparatus.

The fused silica 0.25-mm-ID capillaries, used initially to hold the droplets, tended to fuse shut whenever they were inadvertently struck by the laser beam. These were replaced by stainless steel needles (0.1-mm ID) which reflected the beam rather than fusing. Whenever a sample burned, the liquid sample in the needle was evaporated by the heat, plugging the needle. A stream of nitrogen was used to purge the system to avoid fires. Since the purpose of the CW laser was to cause detonation rather than combustion by rapid heating, the use of an inert atmosphere did not significantly compromise the objective of the experiment. It was observed that slurry droplets became white not at the point of laser impact in less than 100 ms.

Drops were frequently knocked off of the needle by gas evolution resulting from sample vaporization. A small stand topped with a lucite pedestal, which could be raised into the laser beam, was built to fit inside the sample chamber so that drops of liquids and small pieces of solids could be held in the beam in some of the later tests.

1.10 Initial Carbon-Slurry Fuel/Additive Test

Initial attempts were made to detonate a mixture of 9:1 carbon slurry fuel/ammonium nitrate. These mixtures seemed to produce sparks when compared to the carbon-slurry fuel alone but did not explode.

The tests were done with drops from stainless steel needles using about one-third of the falling-drop volume. At short pulse times (100 ms) heat emissions, as measured by the oscilloscope trace, rose and held nearly constant for the duration of the laser radiation input. This may have been due to evaporation of the JP-10 fuel in the slurry. At longer times (1000 ms) the heat output was low at first and then jumped sharply. This may have been due to completion of evaporation followed by heating of the carbon residue. Multiple tests appeared to confirm that the heat output curve was roughly reproducible. Examples are shown in Figures 2A and 2B. It should be noted that the diode had a 15V saturation limit which was reached during one of the heat "spikes," causing the flat spot in Figure 2B.
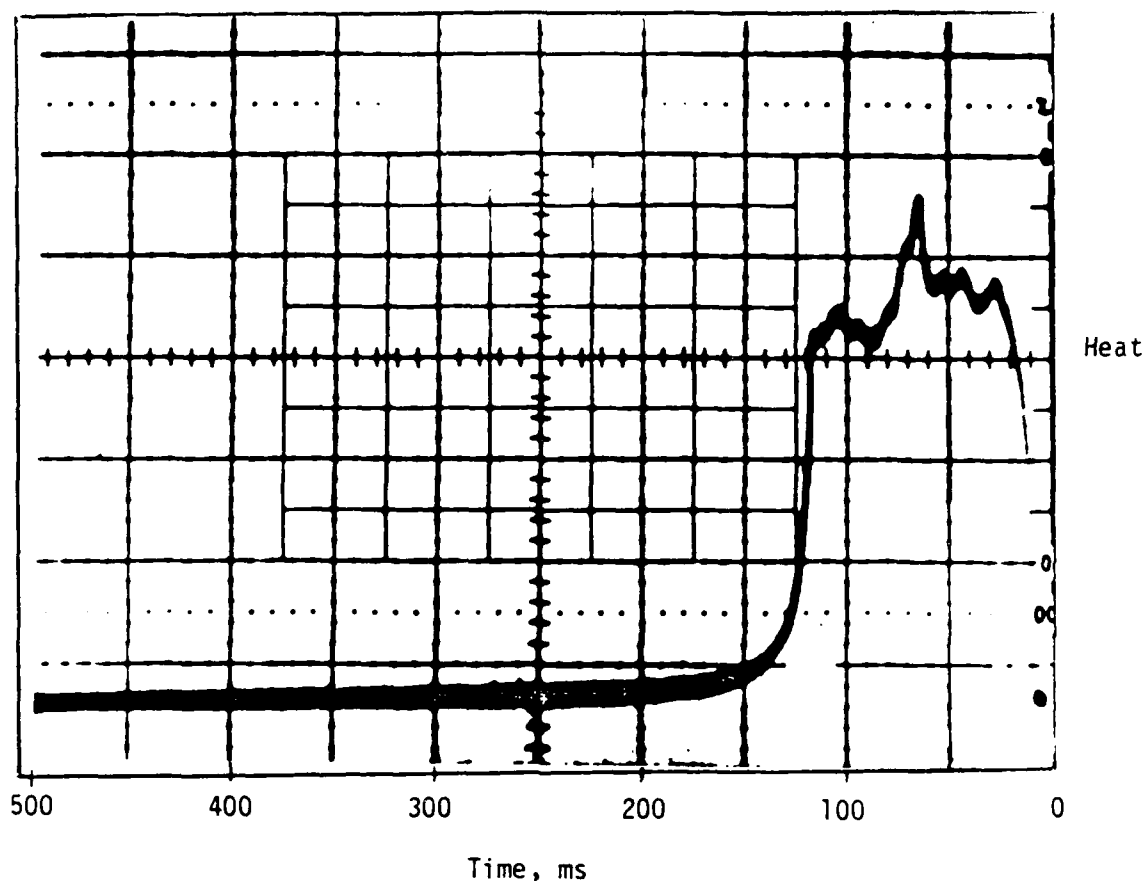
15

Heat

Time, ms

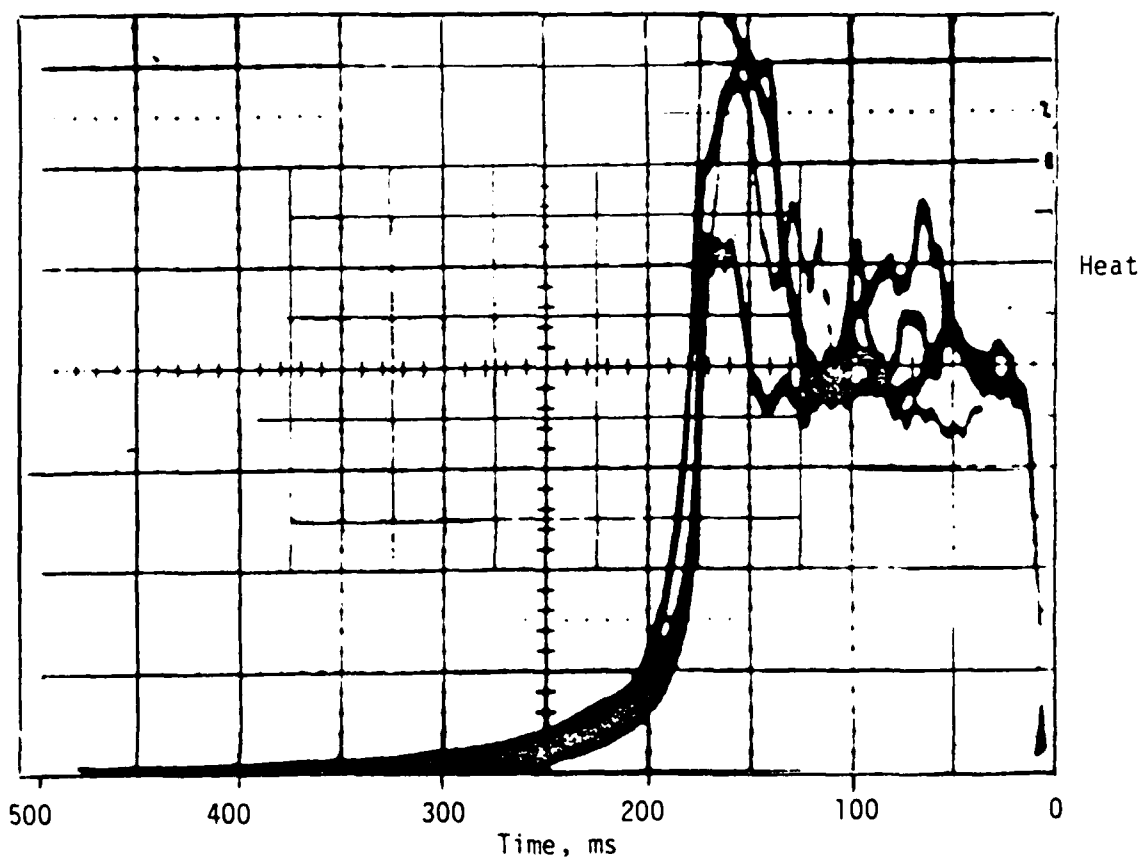FIGURE 2A.   CARBON SLURRY FUEL, 100 MS LASER PULSE TIME

Heat

Time, ms

FIGURE 2B.   MULTIPLE EXPOSURE, CARBON SLURRY FUEL, 150 ms LASER PULSE TIME

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Similar experiments with carbon slurry fuel/TNT/NH$_4$NO$_3$/H$_2$O mixtures showed essentially the same behavior. TNT could not be exploded under these experimental conditions. A typical heat trace is shown in Figure 3.

One test with methanol added to the carbon slurry suggested that evaporation took place, but the heat output was lower, perhaps due to the lower boiling point of methanol. (Figure 4).

1.11 Pure Additive Tests

Since there is no evidence to indicate that detonation was occurring using the additive-fuel mixtures, it was decided to try to detonate pure additives. Two series of tests were conducted to see if pure additives could be caused to explode by laser irradiation using the 50 W CW CO$_2$ laser. In the first series the additives, most of which were solids, were dissolved in solvents, either acetone or water, and suspended from a needle or soaked onto paper and held in an argon atmosphere in the laser path. None of the additives exploded. Several didn't even burn rapidly in the argon atmosphere at laser irradiation times up to 1000 ms, possibly due to the lack of stoichiometric amounts of oxygen.

The drops were frequently knocked off the needle by gas evolution resulting from solvent evaporation. Solvent evaporation dominated the reaction sequence. Irradiation of pure additives was needed.

A small stand topped with a Lucite pedestal was built to fit the laser sample chamber so drops of pure liquids and small amounts of pure solids could be placed in the laser beam.

The second series of tests were conducted to see if pure additives could be detonated by laser irradiation using the 50 W CW CO$_2$ laser under solvent-free conditions. Several additives burned, but none exploded. None continued to burn under argon after the laser pulse stopped, again possibly due to the absence of oxygen, but also possibly because heat loss was too rapid. Some melted or gave off smoke. Tetryl, a high explosive, was the most active material.

A summary of the result of the pure explosive tests is listed in Table 2.
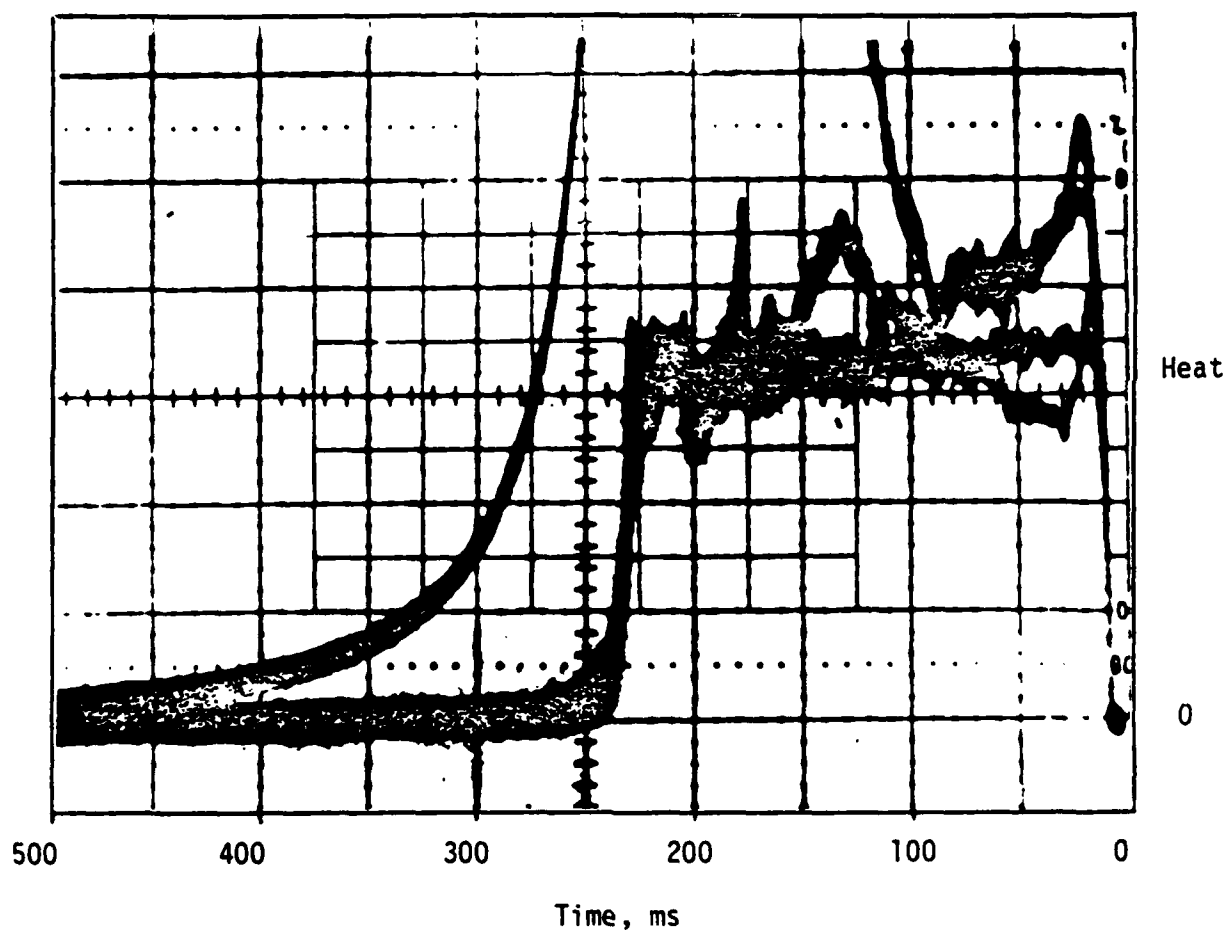
FIGURE 3.   CARBON SLURRY FUEL/NH_4NO_3/TNT/H_2O, LASER PULSE TIME = 200 ms
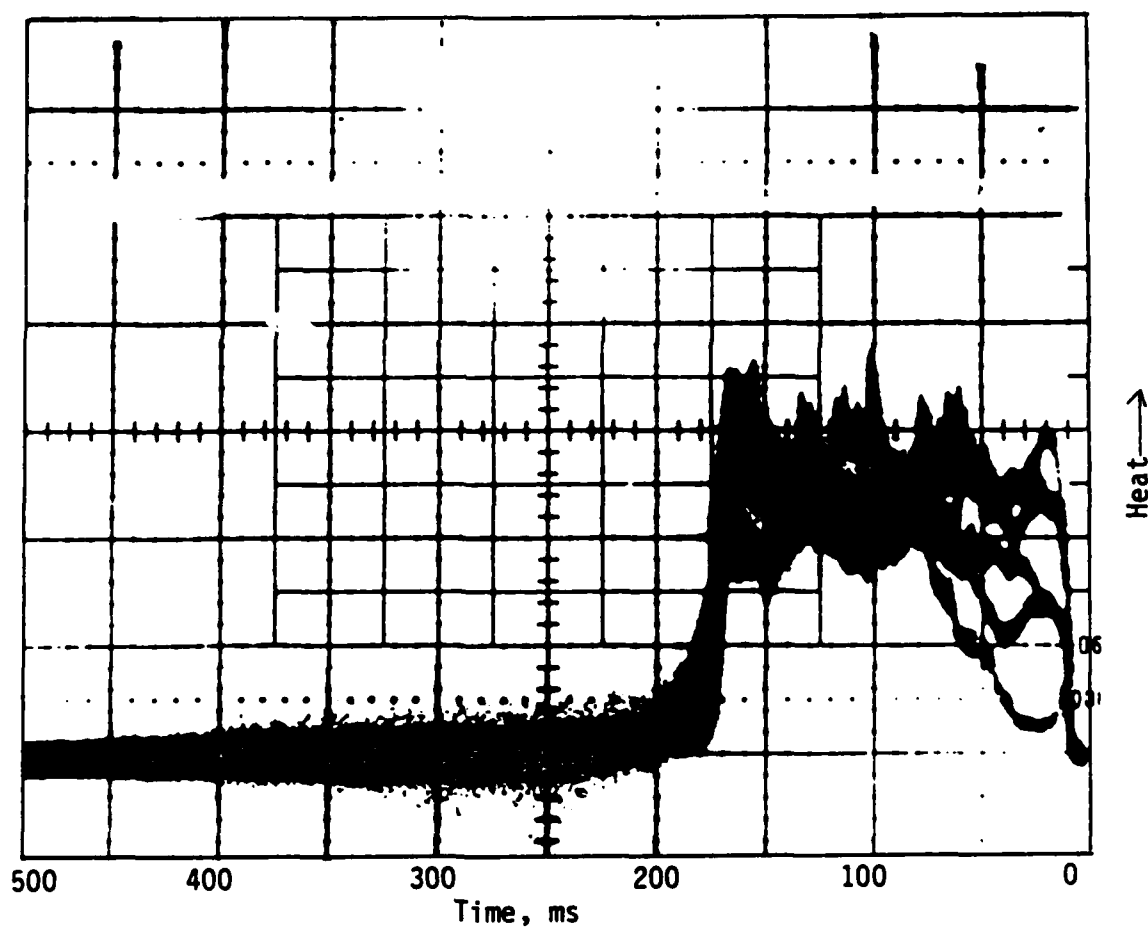
FIGURE 4. CARBON SLURRY FUEL/MeOH LASER PULSE TIME = 100 ms

TABLE 2. SUMMARY OF DETONATION STUDIES ON PURE EXPLOSIVES USING A 50 CW CO_2 LASER UNDER ARGON

| Sample | Description of Sample Behavior Vs Laser Exposure Time | |
	100 ms	1000 ms
Ammonium Nitrate	Melted, white to brown	Visible flame
Ammonium Perchlorate	No chemical reaction	Visible flame
Nitromethane	Gas evolution, flame	Visible flame
Picric Acid	No chemical reaction	Path melts through sample, no fire
Sodium Azide	Water vaporizes	Path melts though sample, no blackening
Tetranitromethane	Gas evolution	Melts, much smoke, no flame*
Tetryl	No chemical reaction	Path melts through sample, blackness
TNT	Melts to brown liquid, fire	Evaporate, no fire
	Melts, black, small flame	Burns rapidly to black residue
		Melts, smoke, no visible flame

*Second exposure of same sample to laser.

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1.12 Additive Tests With Added Carbon-Slurry Fuel

Tests using the 50 W CW CO_2 laser under argon were performed on a 1:1 mixture of each additive with the carbon slurry fuel added to improve heat adsorption. A summary of the results is listed in Table 3. Ammonium perchlorate was by far the most reactive under these conditions, but none of the additives exploded when the carbon-slurry fuel was added to make the adsorption of heat more efficient.

1.13 Initial Pulsed Laser Tests

The purpose of the pulsed laser tests was to see if detonation could be accomplished by generating a shock wave in the sample.

In order to contain the shock wave long enough for it to pass through the sample, it was necessary to confine the sample. Each sample was packed into the narrow end of a disposable glass pipet and compressed. The sample was then pushed 1 mm beyond the tip of the tube and coated with either sodium silicate solution, Aquadag (a slurry of carbon in water), or carbon-slurry fuel. This produced a cylindrical sample about 5 mm long by 1 mm diameter. The laser beam was aimed at the 1-mm tip extending beyond the glass pipette.

Each sample of pure explosive was prepared with no coating and with each of the three coatings used above. Each was exposed to the pulsed laser in air. The results are listed in Table 4.

Even with an empty glass sample tube, a loud snap and a white spark were produced. In some cases the glass tube was broken. When the carbon-slurry fuel was tried with and without an additive, repeated laser pulses drilled a small hole in the sample. There was no evidence of any other reaction - no smoke or flame.

In most cases, the sample was knocked off of the top of the tube. Sample which survived in the tube was unchanged or was blackened on the top surface. The glass was frequently broken. However, there was never any evidence that a sample had detonated.

A sensitive calorimeter was placed 10 cm from the sample. The chemical energy in the small (1.5 mg) samples was about equal to the amount

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TABLE 3. SUMMARY OF DETONATION STUDIES ON 1:1 MIXTURES OF EXPLOSIVE AND CARBON SLURRY FUEL USING A 50 W CW CO₂ LASER UNDER ARGON

Sample	Description of Sample Behavior Vs Laser Exposure Time	
	100 ms	1000 ms
No additive	Slight glow	Orange glow, char
Ammonium nitrate	Orange glow	White glow, no flame
Ammonium perchlorate	-	Orange sparks, little smoke
Nitromethane	-	Orange glow
Picric acid	-	Much smoke, fizzed
	-	Little smoke, char residue*
Sodium azide	-	Flame, sustains combustion beyond laser exposure
		Char glows but doesn't burn*
Tetryl	-	Orange glow, much green smoke
		Char burns a little after laser* exposure
TNT	Slight glow	Orange glow, some smoke

*Second exposure of same sample to laser.

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TABLE 4. SUMMARY OF RESULTS ON COATED EXPLOSIVE SAMPLES USING Nd-YAG LASER

Sample	Coating None	Aquadag	Carbon Slurry Fuel	Sodium Silicate	Results
None (glass tube)	X				Broke glass, bright flash
Ammonium nitrate	X				Sample knocked off
		X			Sample knocked off
			X		White sample residue
				X	Sample knocked off, black Sample residue
Ammonium perchlorate	X				(No test)
		X			Sample unaffected
			X		Broke glass, sample knocked off
				X	Sample knocked off
Picric acid	X				(No test)
		X			No reaction
			X		Sample knocked off
				X	(No test)
Sodium azide	X				Sample knocked off, glass broken
		X			No reaction
			X		Sample knocked off
				X	Broke glass
Tetryl	X				Broke glass
		X			Sample knocked off
			X		Sample knocked off
				X	Sample blown out of tube
TNT	X				Sample knocked off
		X			Sample knocked off
			X		Sample knocked off
				X	Sample knocked off, broke glass

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of energy reflected from the sample by the laser striking it. Initially,
the calorimeter could not be used to differentiate between a sample detonation
and the laser reflection.

There did not seem to be much difference between coatings. The
coating did not improve sample integrity by holding the powder samples together.
Sodium silicate reacted with some of the samples. Aquadag seemed to decrease
the response of the sample to the laser. The carbon-slurry fuel itself appeared
to be the best coating for this purpose.

1.14 Pulsed Laser Tests with Glass Enclosed Samples

A second set of samples was prepared by enclosing the sample inside
glass tubes and sealing each end with sodium silicate. In these tests the
laser had to pass through the glass tube wall to strike the sample.

The calorimeter was equipped with a narrow band-pass filter to
remove any reflection of the 1.06 μm laser radiation.

The results of these tests are listed in Table 5. Using samples
prepared in this way there was no evidence of sample reaction. Hitting the
sample tube with the laser invariably broke the glass. It is possible that
most of the laser energy was reflected off the curved glass surface. Flat
plate-sample holders may have been an improvement but were not tried.

There was no significant difference between calorimeter readings,
either between sample types or sizes. The reading levels were well below
what would be expected if a chemical reaction occurred (10^{-4}J). This also
suggests that no explosions took place.

1.15 Flat-Flame Combustion Experiment

Small amounts of each additive were dropped into a flat-flame (Meeker
burner), enclosed in a glass tube to remove drafts, to see which reacted
most rapidly in an actual combustion environment. Sodium azide particles
caught up in the flame draft burned so rapidly that they appeared to burst
under these conditions. Based on this observation, sodium azide might be
the most effective of the additives tested for promoting secondary atomization.

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TABLE 5. SUMMARY OF RESULTS USING Nd-YAG PULSED LASER AT 1 JOULE/25 MS WITH SAMPLES BEHIND GLASS PLUGGED WITH SODIUM SILICATE

Sample	Results	Calorimeter Reading X10^{-6}J
Sodium chloride	Broke glass	1.0
Sodium silicate	Broke glass	1.1
Carbon slurry fuel	Broke glass	0.9
Ammonium nitrate	Broke glass	1.0
Ammonium perchlorate	Broke glass	0.8
Picric acid	Broke glass, yellow residue present	0.9
Sodium azide	Broke glass	1.1
Tetryl (small sample)	Broke glass, some residue, no explosion	1.1
Tetryl (medium sample)	Broke glass, some residue of explosive	1.0
Tetryl & carbon slurry fuel	Broke glass	1.0
TNT	Broke glass	1.1

2. Discussion

The results of this investigation are negative in that none of the "explosive" additives screened promoted secondary atomization of a carbon-JP10 fuel slurry droplet. Due to the brief nature of this investigation, it bears consideration whether the results are negative on theoretical (mechanistic) principles or for lack of sufficient experimental technique (laser intensity).

By definition secondary atomization refers to the break-up of liquid (slurry) fuel droplets in hot gases due to internal vaporization. Based on C. K. Law's investigation[9,10], microexplosions of multicomponent fuel droplet can be explained through a diffusion-limit model. The primary requirements are:

- Two miscible liquids of widely varying volatility
- A concentration of the high boiling, less volatile component on the droplet surface on heating
- A high droplet temperature controlled by the surface composition
- A high Lewis number providing more rapid heat transfer than mass transfer within the droplet
- Superheating of the high volatile component
- Homogeneous nucleation with rapid gas generation from the droplet interior, rupturing the droplet into smaller droplets.

Since this mechanism depends on the existence of a steep concentration gradient it is more likely to occur for a droplet with minimum internal circulation.

In the present program, the premise was maintained that instead of using a wide volatility difference in two miscible liquids to generate internal droplet pressures, one might incorporate an explosive and cause the decomposition of the explosive to create the internal fragmentation force. The results suggest that it apparently was not possible to cause the explosive to detonate and generate gas within the droplet. In hindsight, one can ask whether this is possible since the laser must initially deposit energy on the surface of the opaque particles. If one follows C. K. Law's mechanism presented earlier, it becomes apparent that the explosive must be maintained

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in the interior of the droplet (on the basis that the gas evolution from the explosive would be entrapped in the surrounding slurry-fuel droplet). If this situation is not achieved then one must question whether homogeneous decomposition can occur (1) deep within a droplet, and (2) sufficiently early in the droplet lifetime. As Law shows in his studies, these two requirements are not always satisfied in miscible multicomponent systems with widely varying volatilities. It would appear that this was also the case when explosives were incorporated into the slurry droplet.

The above situation notwithstanding, it is also possible that the experimental approach used in these studies was flawed. Laser radiation was selected as a means of providing high energy in a short time to minimize competition between heatup rates and devolatilization rates. It seems likely that laser radiation did not promote intense internal circulation within the droplets so that vaporization resembled surface distillation rather than batch distillation. In subsequent programs a different experimental design should be considered, one in which convection heating would be more predominant, such as in a drop-tube furnace.

3. Explosive Additive Conclusions

The principal conclusion of this work is that, except under extraordinary circumstances, typical "explosive" compounds do not explode, and that the hypothesized method of achieving seondary atomization by adding explosives in carbon-slurry fuel combustion may not be technically feasible.

Different compounds are more reactive under the various reaction conditions tried, but no instance of actual detonation was observed in this work. The actual conditions in a jet engine combustor were not simulated so no recommendation for an additive to test under these conditions can be made.

4. Postscript

At the conclusion of this study, we had the opportunity to discuss the results with Dr. Ardeen Walters of Florida Power and Light Corporation,

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Juno Beach, Florida.[29] Dr. Walters has examined this subject of secondary atomization using explosives to improve the atomization of coal-water slurry droplets. It is quite possible based on his experience and calculations that the particle size of many explosives may need to be too large to detonate and shatter droplets. In the case of potassium picrate, he estimates that a crystal smaller than 300 μm, about 10 micrograms, requires a mean induction time of over one second.[30] Hence, a slurry droplet of potassium picrate in a fuel would not have sufficient time to detonate in the milliseconds in a gas turbine combustor. Each explosive will have its own requirements for detonations. It is possible that those selected for this study fall into that class and will not detonate if smaller than 200-300 μm. In essence, the requirements for additive detonation include: critical mass, critical density, size, and induction time. Any continuing program in this area should attempt to keep these criteria in mind.

IV. VOLATILE ADDITIVE STUDIES

1. Results and Discussion

Occurrence of microexplosion can be facilitated through several major factors. First, the volatility differentials between the more and less volatile components should be as wide as possible in that the less volatile component is needed to drive up the droplet temperature while the more volatile component is needed for its ease to spontaneously gasify. Second, internal gasification is facilitated by the presence of particles, as in slurries, which provide heterogeneous nucleation sites; without such sites the droplet would have to be heated to much higher temperatures to initiate homogeneous nucleation. Third, the intensity of microexplosion appears to be higher for emulsions, with the volatile component being the dispersed phase, than for a miscible mixture. The reason is that the dispersed micro-droplets provide much larger mass elements for the instantaneous conversion to gas.

The carbon slurry of interest is made of carbon black mixed in JP-10 fuel with the aid of a surfactant of proprietary nature and composition. Since JP-10 is a pure fuel, and if we temporarily disregard the influence

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of the surfactant, microexplosion of their slurry droplet is not favored. Therefore, in order to induce microexplosion, additives are needed to make the liquid fuel multicomponent.

1.1 Droplet Explosion Temperature Studies

There are two characteristic droplet temperatures which are of importance in the present phenomena. The first is the maximum attainable droplet temperature. For a droplet consisting of only JP-10 and the carbon powder, this temperature should be limited by the boiling point T_b of JP-10, which is 182 C at atmospheric pressure. This temperature should not be influenced much in the presence of surfactants and small amounts of volatile additives.

The second characteristic, T_e, is the one corresponding to the state at which internal gasification is initiated. For a given mixture composition at any location within the droplet, T_e should be bounded by the boiling point and the limit of superheat, T_e, for that mixture composition; at these two temperatures heterogeneous and homogeneous nucleation are respectively initiated.

Based on the above discussions, in order for internal gasification and thereby microexplosion to take place, a minimum requirement is $T_e < T_b$. For These two values, T_b is reasonably well defined, allowing for possible influences due to additives and surfactants. The value of T_e, however, is not known and needs to be experimentally determined.

The apparatus used to determine T_e is shown schematically in Figure 5. Here an upwardly-directed positive temperature gradient is established in a liquid column by using electrical heating tapes. At the bottom of the column a droplet of the test liquid, which is immiscible with the column liquid and also has a lower density, is introduced and rises slowly and steadily due to buoyancy. For a sufficiently small droplet, say around 1 mm in diameter, the droplet is in perpetual thermal equilibrium with the column such that its temperature can be approximated by the local column temperature. Thus, when the droplet reaches T_e and explodes, the value of T_e can be determined by simply measuring the temperature of the column at which explosion takes place. The crucial feature of this arrangement is that, except for the carbon
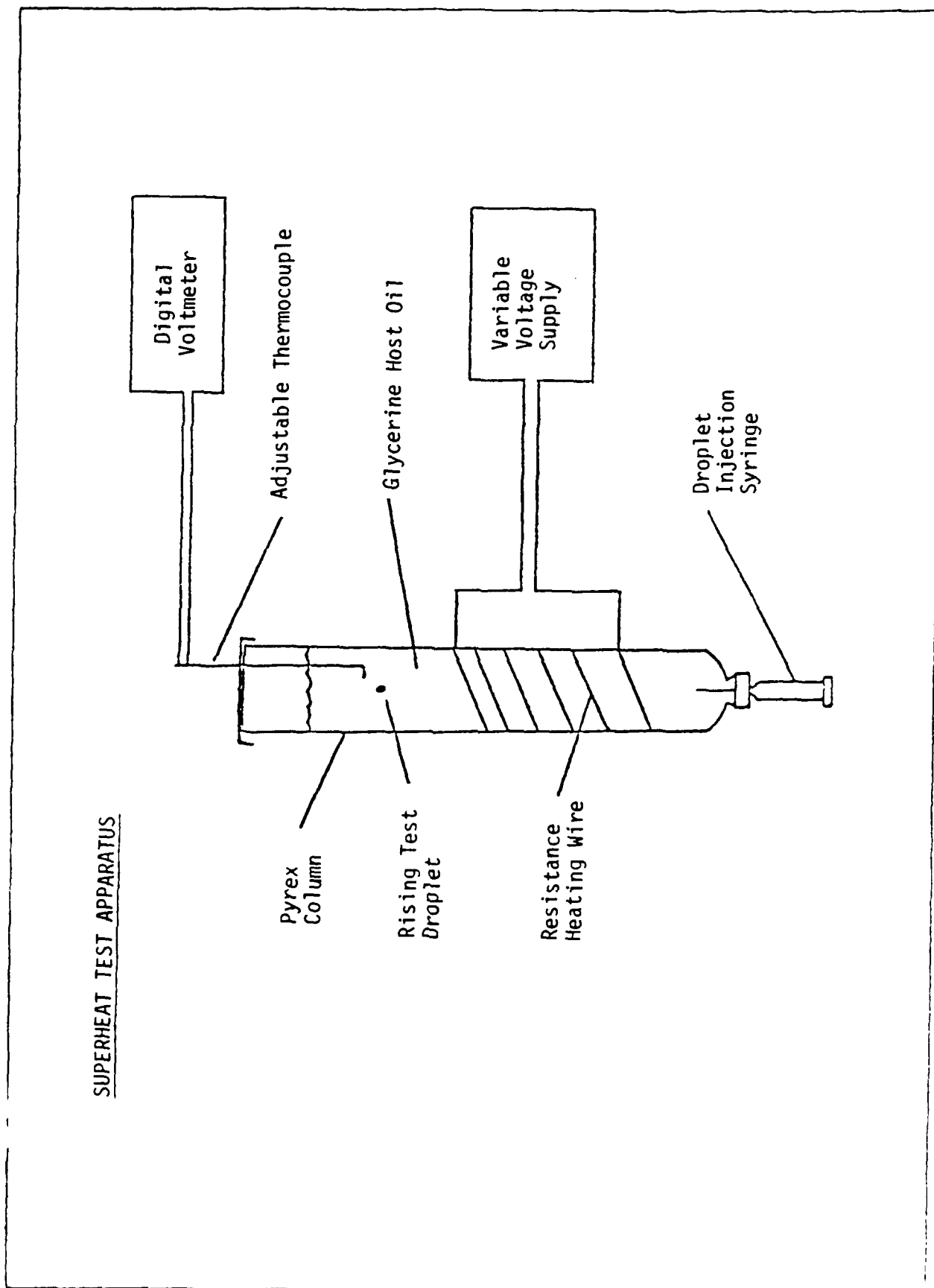
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SUPERHEAT TEST APPARATUS

Digital
Voltmeter

Adjustable Thermocouple

Glycerine Host Oil

Variable
Voltage
Supply

Droplet
Injection
Syringe

Pyrex
Column

Rising Test
Droplet

Resistance
Heating Wire

FIGURE 5. SCHEMATIC OF APPARATUS USED TO MEASURE EXPLOSION TEMPERATURES OF THE TEST FUELS

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powders, no additional solid surfaces, such as those of a thermocouple, are introduced into the test droplet to falsify the nucleation process in the act of temperature measurement.

Figure 6 shows the explosion temperatures of JP-10 with various concentrations of carbon slurry. The limit of superheat for pure JP-10 cannot be determined because it exceeds the boiling point of the column liquid, glycerin. The most interesting result here is the reduction of T_e with the addition of small amounts of carbon slurry, although this reduction rapidly approaches an asymptotic value of about 240 C. Thus, increasing the carbon loading will not further reduce the explosion temperature.

Figures 7 to 10 show the explosion temperatures of cyclohexane, decane, octane, and a 50-50 mixture of heptane-hexadecane with small amounts of carbon slurry addition. The rapid initial decrease followed by an asymptotic behavior is again observed. Note that this explosion temperature is intermediate of the limit of superheat temperature and the boiling point. Furthermore, this asymptotic temperature can be lowered to the boiling point of JP-10, 182 C, only for fuels whose boiling point is less than that of octane.

Figure 11 shows the explosion temperatures of carbon slurry (22 percent carbon loading by mass) with addition of small amounts of pentane, hexane, and heptane. Although the addition of these volatiles generally lowers the explosion temperature, the extent of reduction is not as large as doping these volatiles with the slurry fuels.

Based on the above results, we conclude that fairly volatile fuel additives are needed to induce microexplosion of the carbon slurry droplet.

1.2 Droplet Combustion Experiments

Although many experiments have been performed on slurry droplet combustion, most of them have adopted the suspended droplet technique. The difficulty with this technique is that the suspension fiber can provide nucleation sites to induce artificial heterogeneous nucleation and thereby droplet microexplosion. Thus, an essential requirement for the study of slurry droplet microexplosion is the use of free droplets. In a previous study of ours, we have used freely falling droplets, although the droplet sizes were too large, of the order of 800 µm. In the present experiments, the initial droplet size was fixed at 340 µm.

SUPERHEATING OF JP-10 FUEL WITH CARBON SLURRY
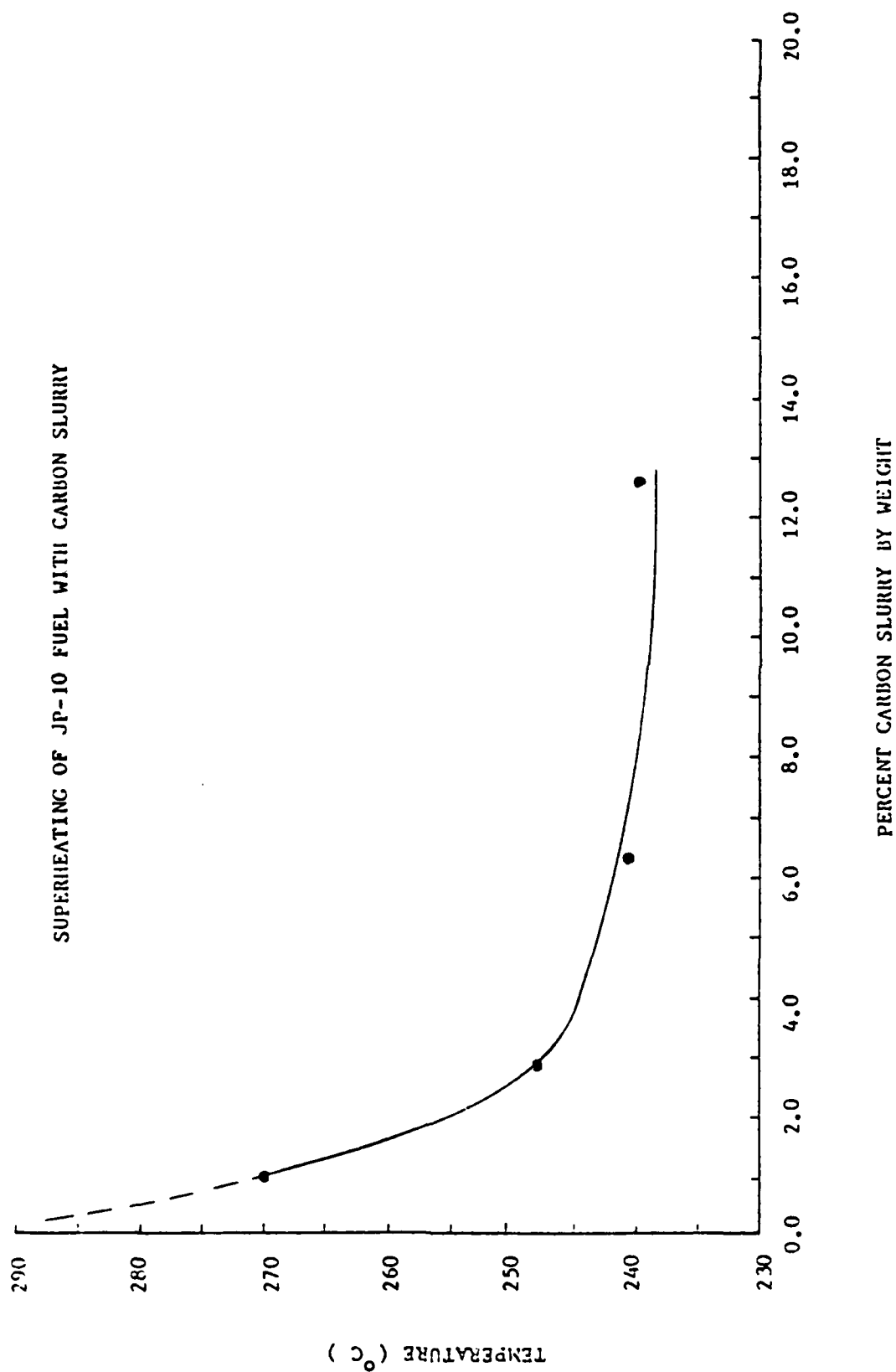
PERCENT CARBON SLURRY BY WEIGHT

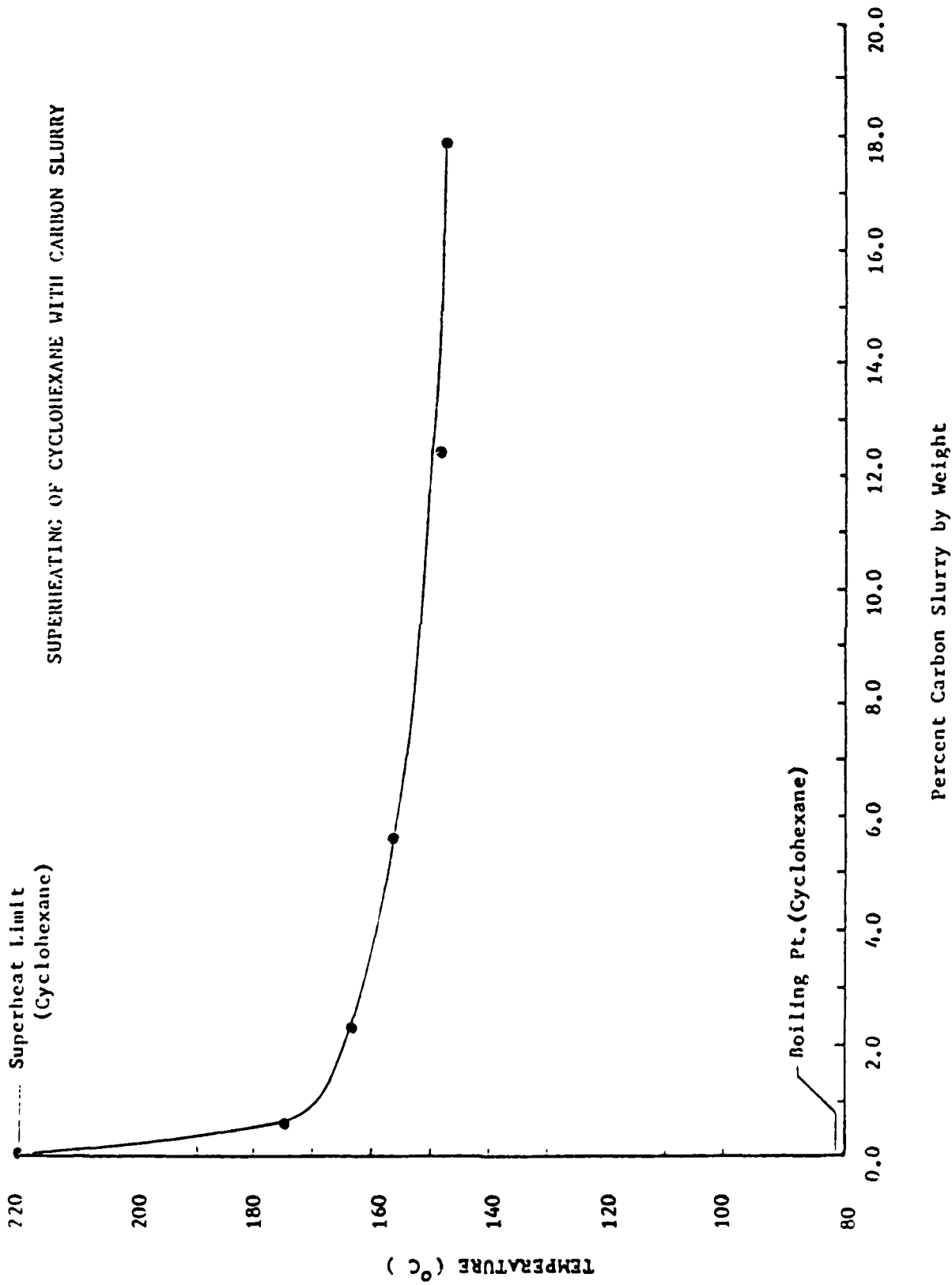FIGURE 6. EXPLOSION TEMPERATURE OF JP-10 CARBON SLURRY FUEL.

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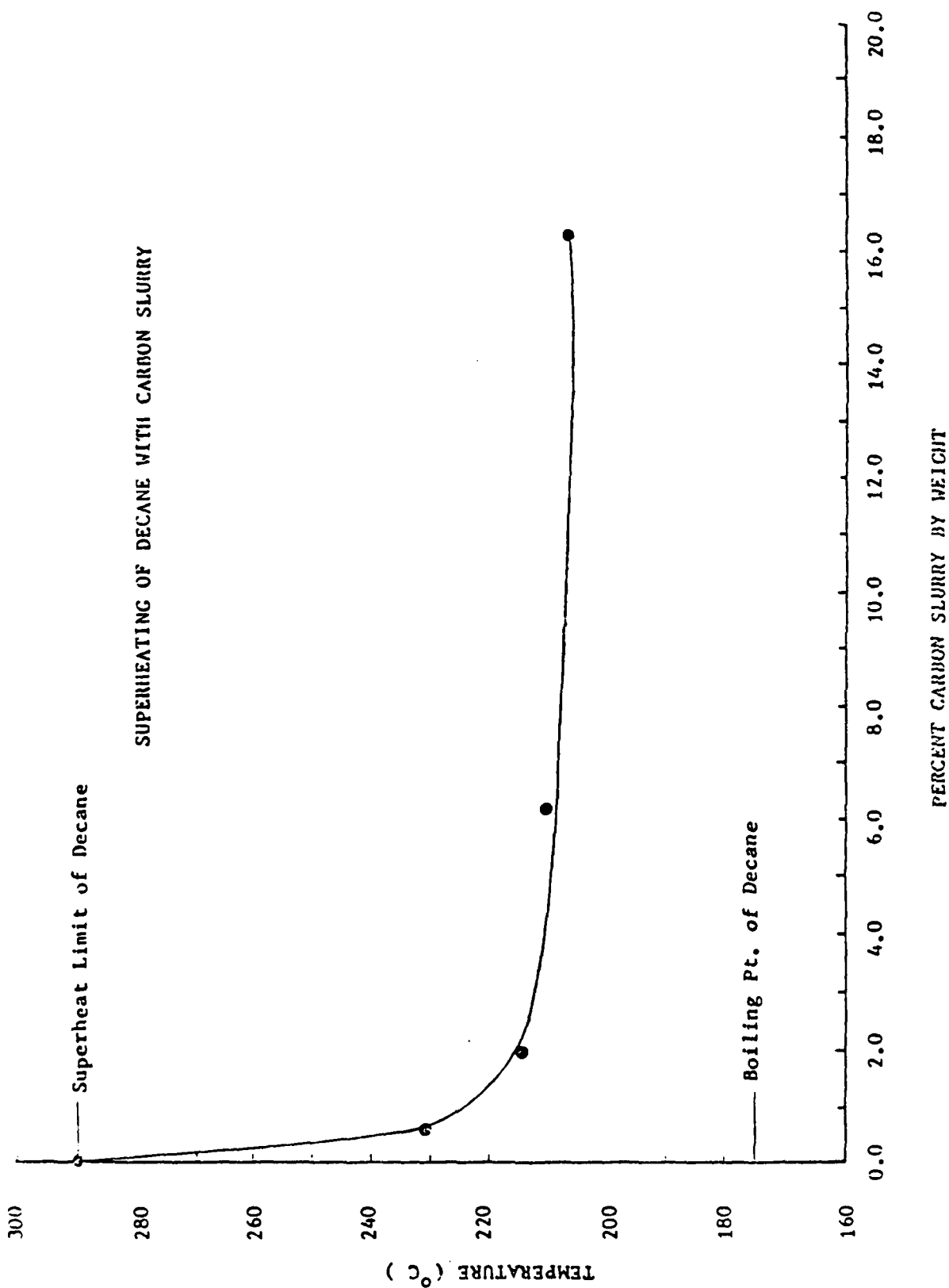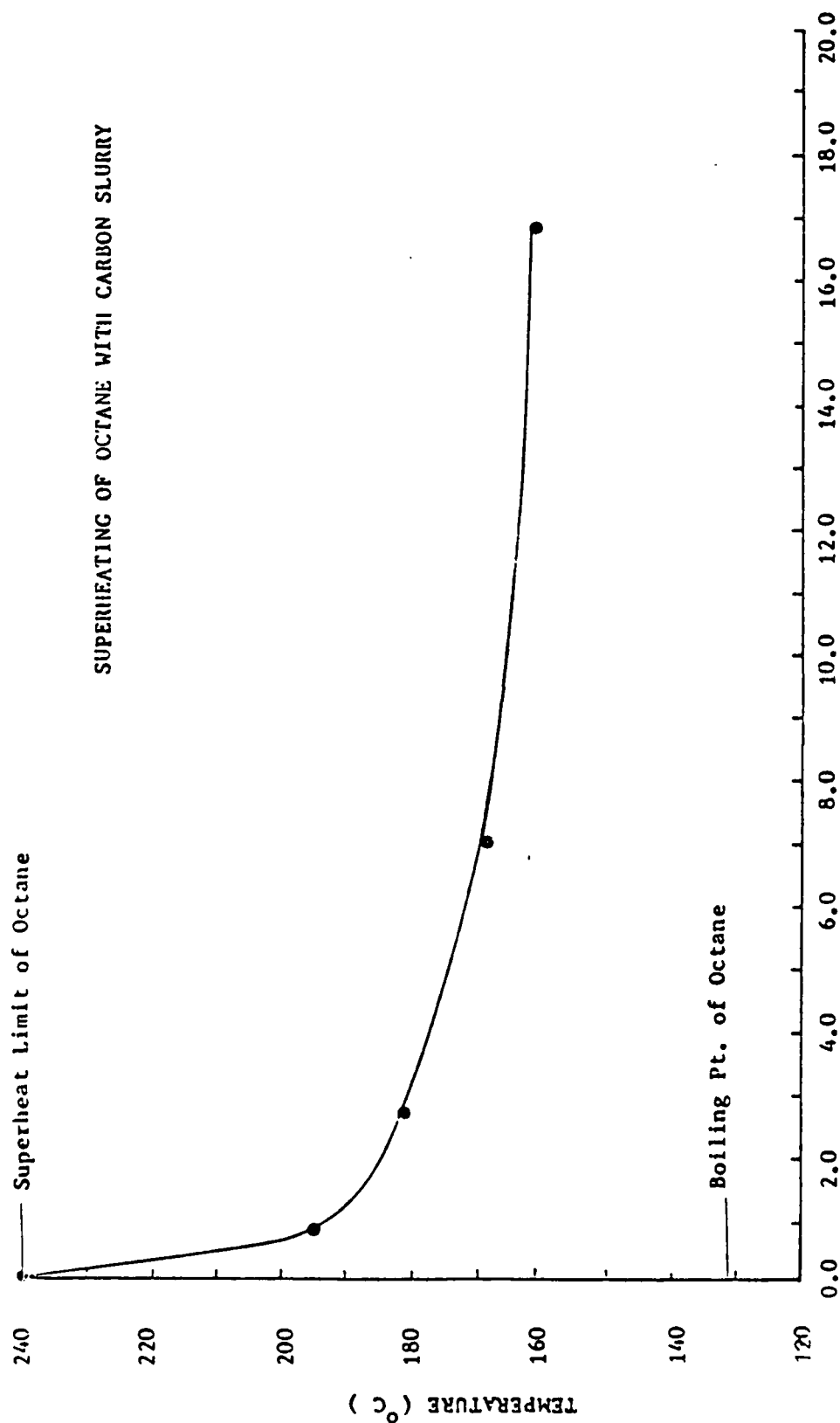FIGURE 7. EXPLOSION TEMPERATURES OF CYCLOHEXANE DOPED WITH CARBON SLURRY

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FIGURE 8. EXPLOSION TEMPERATURES OF DECANE DOPED WITH CARBON SLURRY

FIGURE 9.   EXPLOSION TEMPERATURES OF OCTANE DOPED WITH CARBON SLURRY

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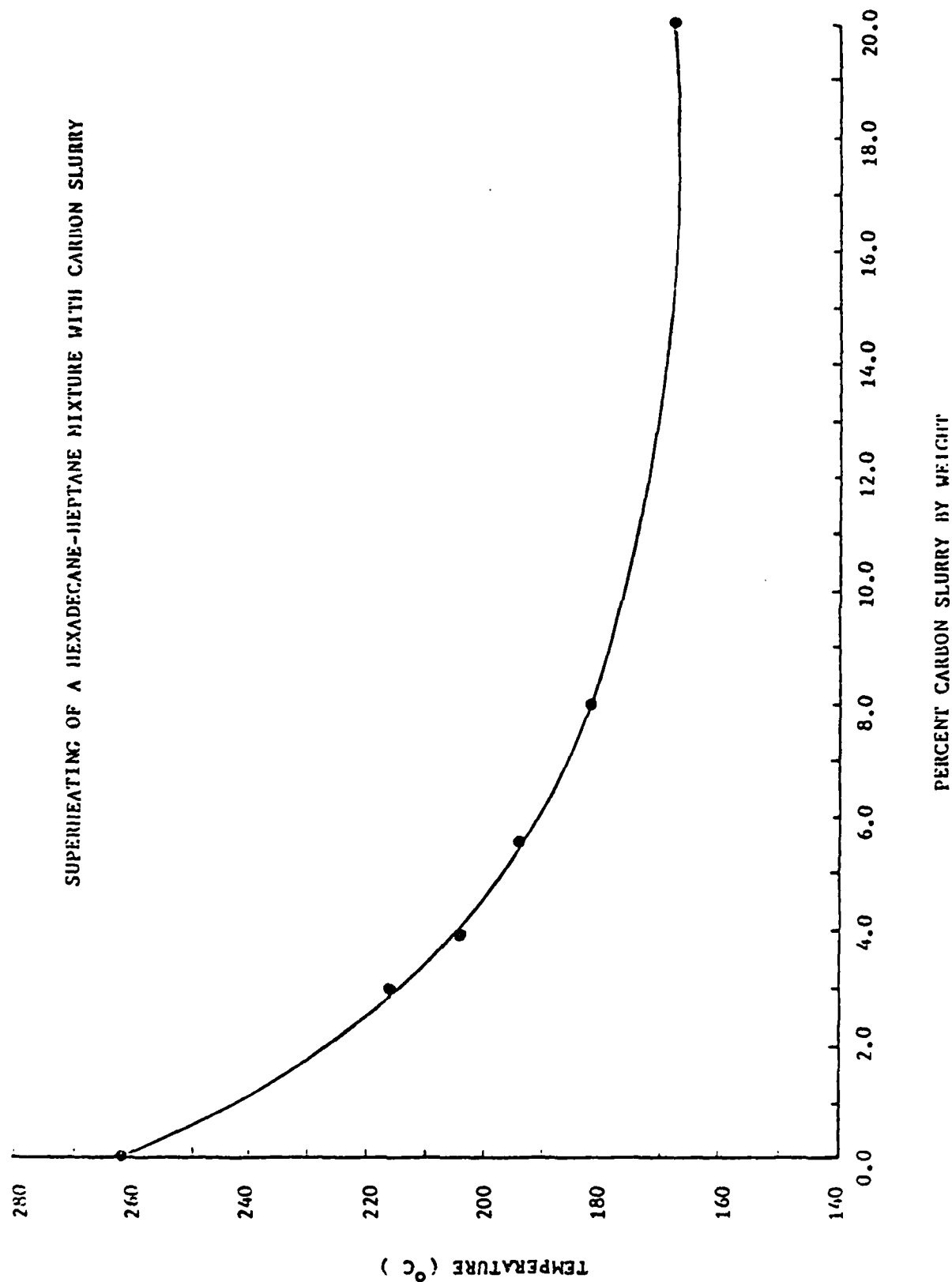SUPERHEATING OF A HEXADECANE-HEPTANE MIXTURE WITH CARBON SLURRY

PERCENT CARBON SLURRY BY WEIGHT

FIGURE 10. EXPLOSION TEMPERATURES OF 50-50% HEPTANE-HEXADECANE DOPED WITH CARBON SLURRY

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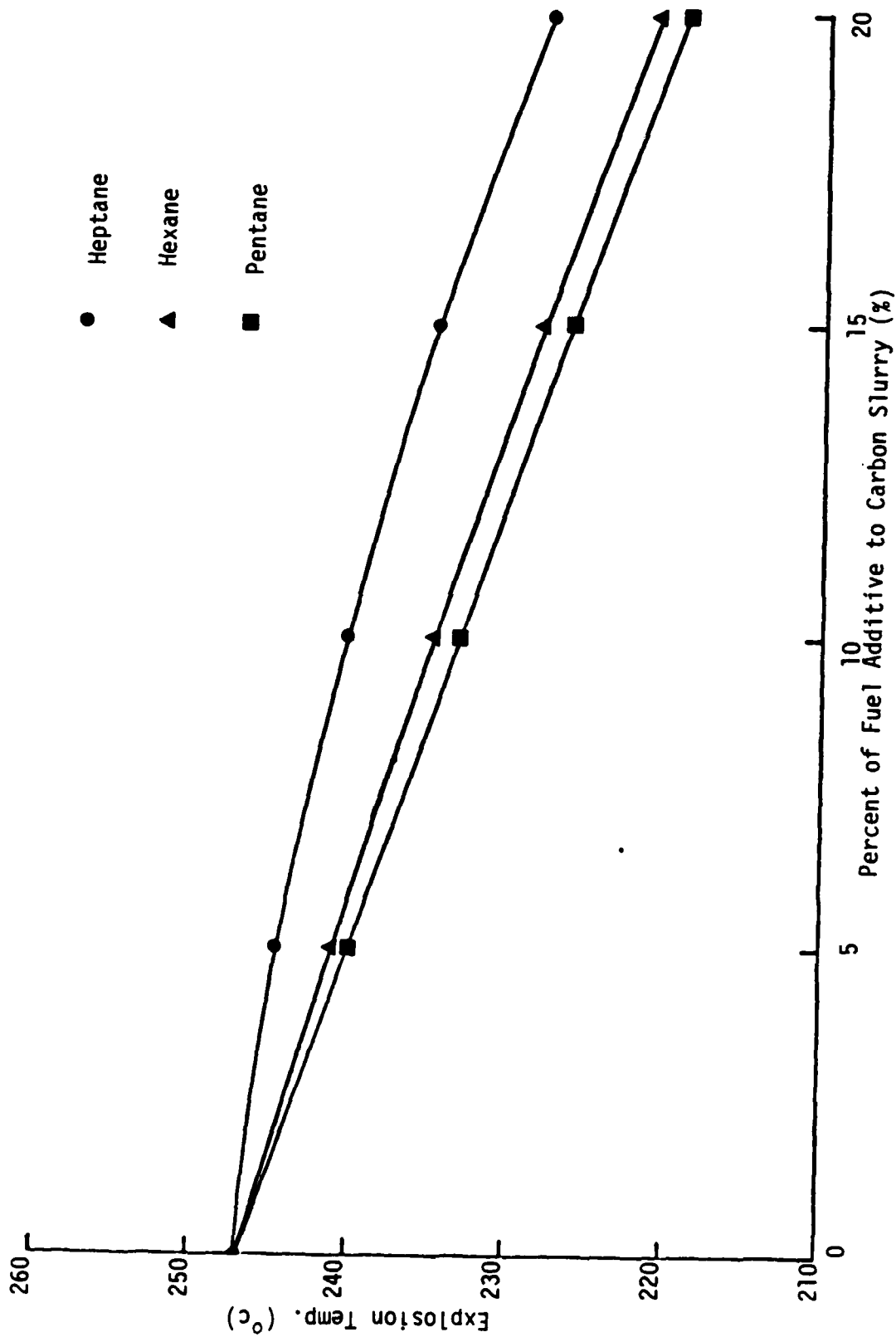
FIGURE 11. EXPLOSION TEMPERATURES OF CARBON SLURRY (22% CARBON BY WEIGHT) DOPED WITH VOLATILE FUELS

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The design of the droplet generator is shown in Figure 12. It basically consists of a diaphragm of piezoceramic crystal pressed against the fuel reservoir. Upon application of an electric pulse, the crystal deforms, therefore squeezing a droplet out of the nozzle. The size of the droplet can be controlled by the size of the nozzle and, to a certain extent, the extent of crystal deformation. The droplet spacing can be controlled by the frequency of the pulses, and can vary from about two droplet diameters to hundreds of droplet diameters; in the latter case the droplets can be essentially considered to be isolated. The droplets then pass through the post-combustion zone of a flat flame burner, ignite, and burn, as shown in Figure 13 for the overall experimental schematic. The temperature and oxygen concentration of the combustion environment can be controlled by changing the compositions of the mixture supplied to the flat-flame burner. All the experimental data to be reported were collected in an environment of 1000 C and 21 mole percent of oxygen.

We found it necessary to project the droplets upward because in the downward orientation slight settlement of the particles tends to block the nozzle. With the present design and arrangement, a stable droplet stream can be produced and maintained for a few minutes. This relatively short operation time does not permit detailed experimentation to accurately time-resolve the droplet combustion process. However, it is sufficient to allow sampling of the fragments due to microexplosion, to be discussed next.

Since the primary objective of the present investigation is to explore and quantify the efficiencies of the various additives in inducing and intensifying microexplosion, a sampling probe (Figure 14) has been developed to collect the fragments produced by microexplosion. The probe consists of a four-stage cascade impactor with vacuum assist and nitrogen cooling. It is intended to collect the fragments just after the occurrence of microexplosion but without further burning of the carbon particles. Thus, the probe is positioned one inch above the state of the microexplosion. Nitrogen is introduced from the walls at the bottom of the probe to cool the incoming gas as well as to quench the carbon particles. A vacuum at the top of the probe is adjusted to pull the particles up through the probe; the pull is optimized such that the particles do not break up upon contacting the cascades.
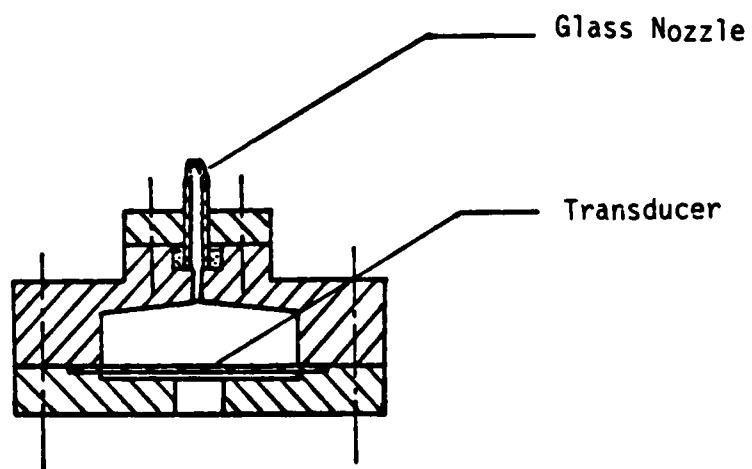
38

FIGURE 12. SCHEMATIC OF DIAPHRAGM-BASED DROPLET
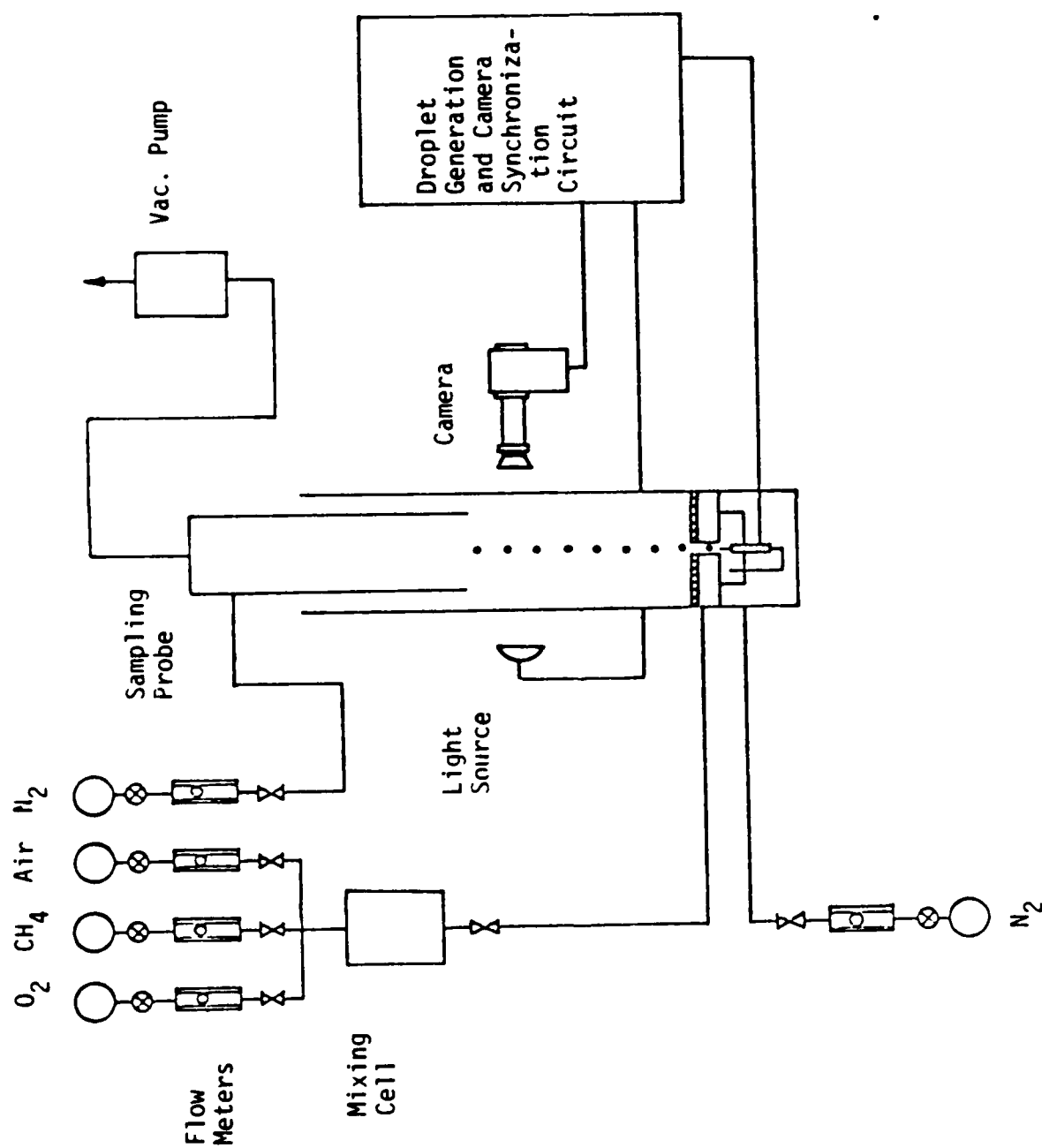GENERATOR FOR SLURRY FUELS

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FIGURE 13. SCHEMATIC OF THE FREELY-FALLING DROPLET COMBUSTION APPARATUS
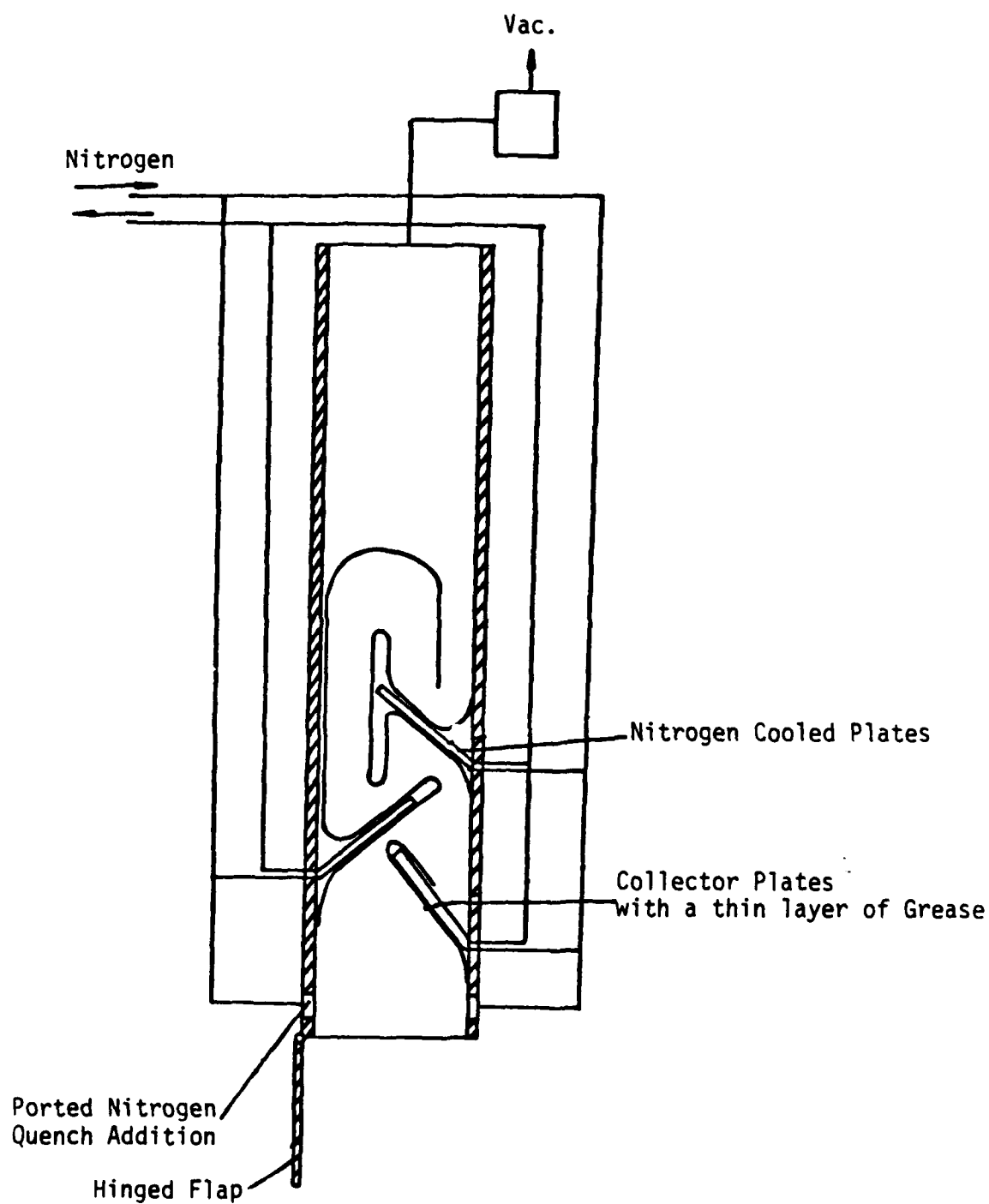
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FIGURE 14.   CASCADE PARTICULATE SAMPLING PROBE

The cascades consist of brass collector plates covered by a layer of high-vacuum grease and attached to nitrogen-cooled hangers. We found that a sampling time of 15 to 20 seconds was optimum to collect sufficient sample for analysis without burning the covering grease.

Design and arrangement decisions as discussed above were all based on the criterion of counting particles larger than 5μm.

The carbon slurry used was supplied by Sun Tech Co. It consists of 56 percent carbon black by weight, with the particle size less than 1μm. This slurry, however, was too concentrated to allow stable generation of the droplet stream. Thus, for all experiments this slurry was diluted by additional JP-10 to yield a final concentration of 22 percent carbon.

Additives tested include pentane, hexane, heptane, ethanol, and ethyl ether, all 5 percent by weight, and 5, 10, and 20 percent water by weight.

Figures 15 to 19 show the present distribution of the fragmented particles in different size ranges. Since the fragmented particles have irregular shapes, the size indicated is the average of the minimum and maximum dimensions of a particle. Thus, this particle size can even exceed the initial droplet size. More than 1700 particles are counted for each additive, implying the statistical significance of the results obtained in this investigation.

Results shown in Figures 15 to 19 are our raw data which is useful for further processing and analysis. In Figures 20 to 22 we have processed these results in log-probability plots, in which the scale for the correct cumulative fraction is probability while the scale for the particle size is logarithmic. These generally straight distribution lines imply that the size distributions are log-normal. Furthermore, in aerodynamic sampling there is an aerodynamic size, called the aerodynamic cutoff size, above which particles cannot enter the sampling probe. This causes the bending of the lines near the upper end of the distribution.

There are two important parameters in the size statistics. The first is the count median diameter (CMD), defined as the diameter at which half of the total number of particles are smaller than it while the other half are larger. The second is the geometric standard deviation σg, defined as the ratio of the cumulative counts of 84 percent to 50 percent; thus, it indicates the steepness of the log-normal plot. A larger σg, that is a steeper slope, indicates a wider distribution of particle sizes. The opposite holds for a smaller σg.
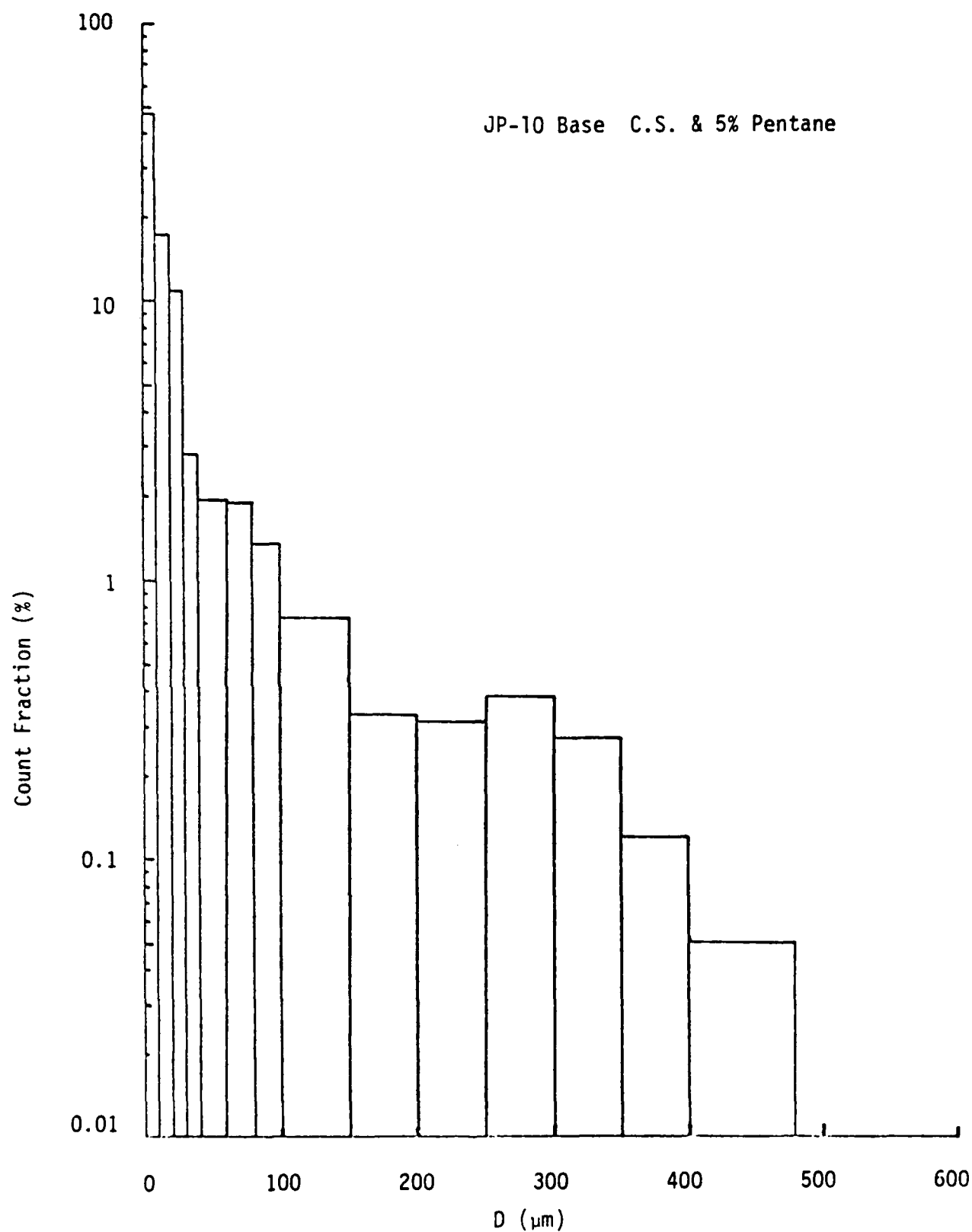
42

FIGURE 15. COUNT FRACTION OF EXPLODED FRAGMENTS OF CARBON SLURRY DROPLETS
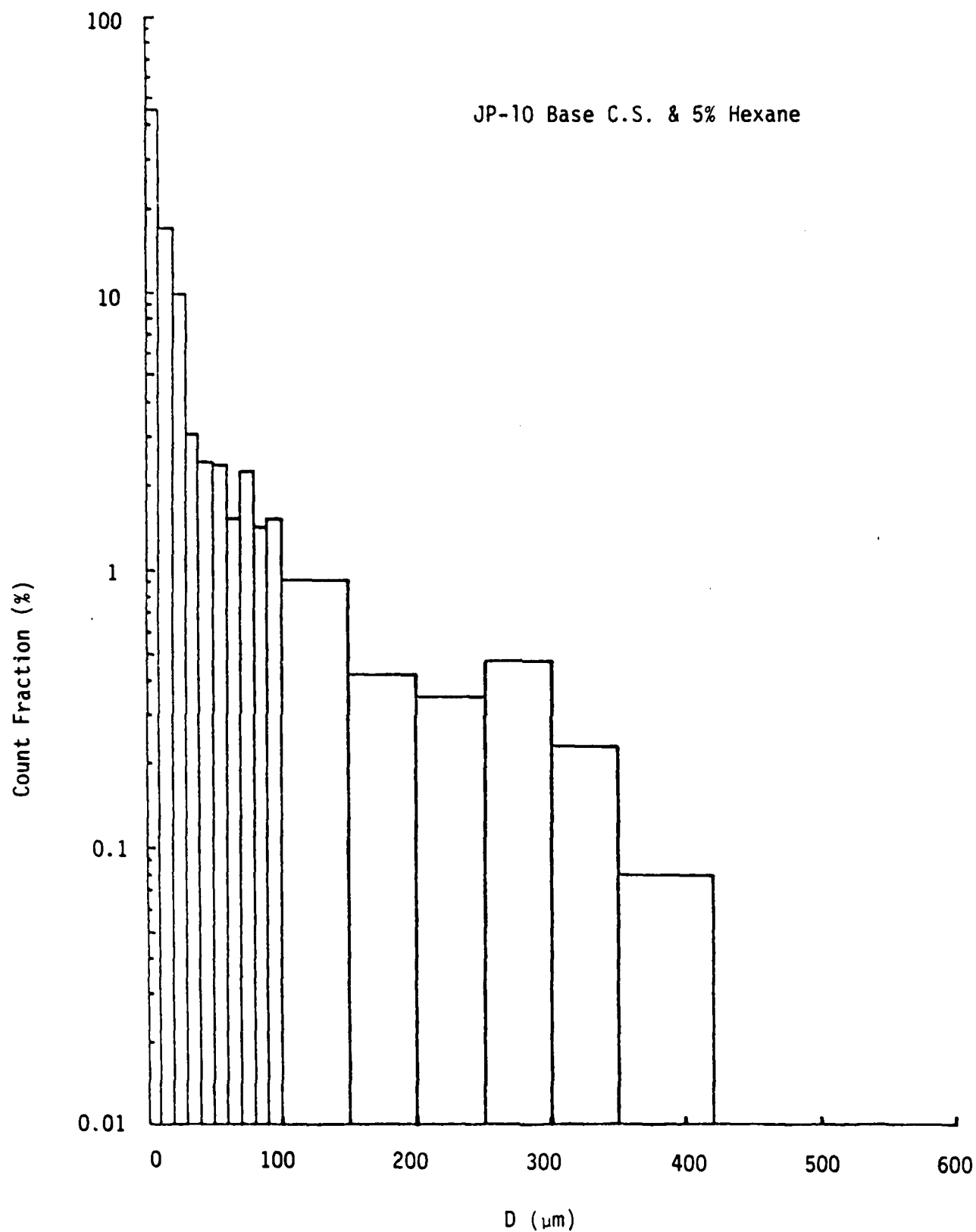DOPED WITH 5% PENTANE

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FIGURE 16.   COUNT FRACTION OF EXPLODED FRAGEMENTS OF CARBON SLURRY DROPLETS
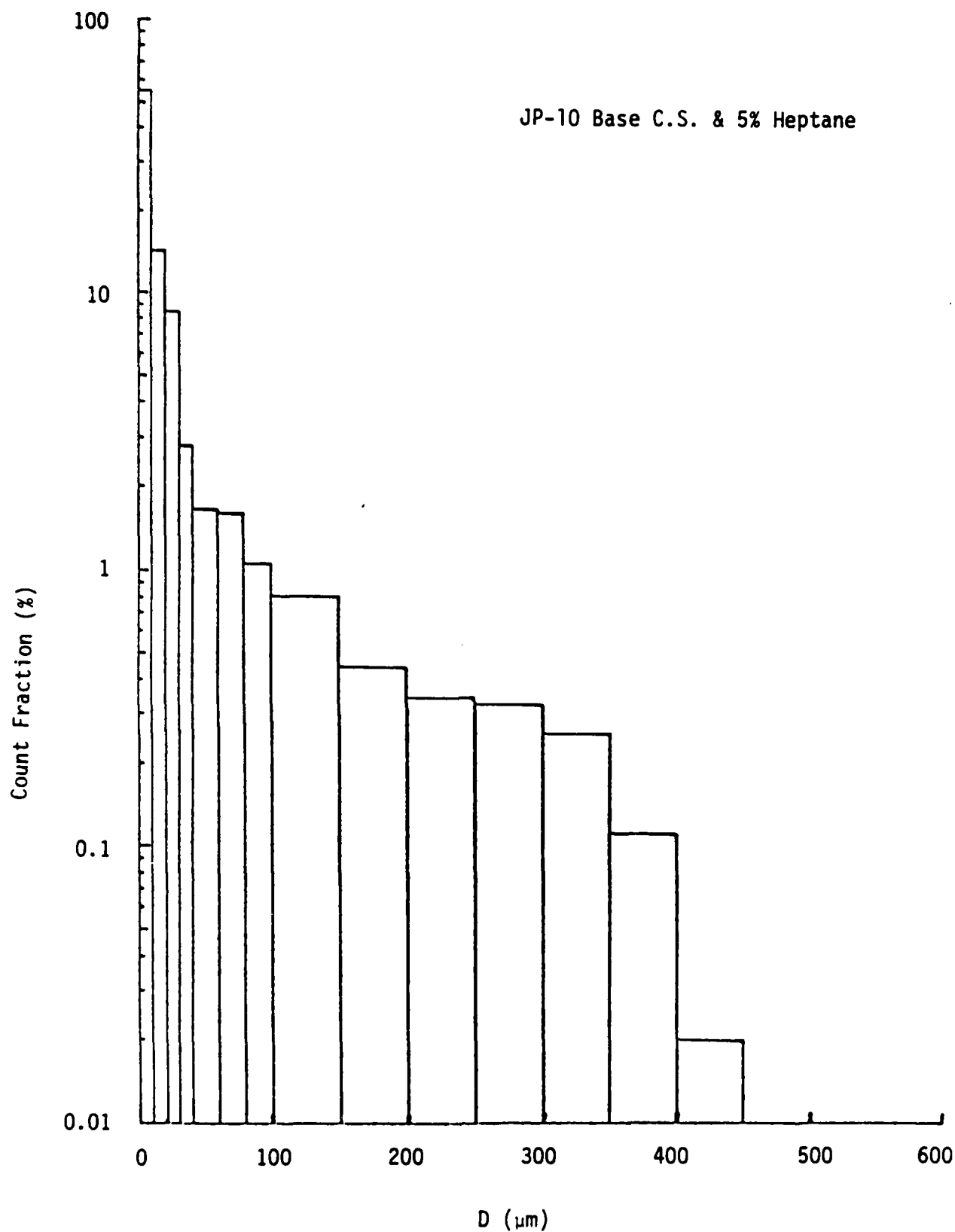DOPED WITH 5% HEXANE

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FIGURE 17. COUNT FRACTION OF EXPLODED FRAGEMENTS OF CARBON SLURRY DROPLETS DOPED WITH 5% HEPTANE
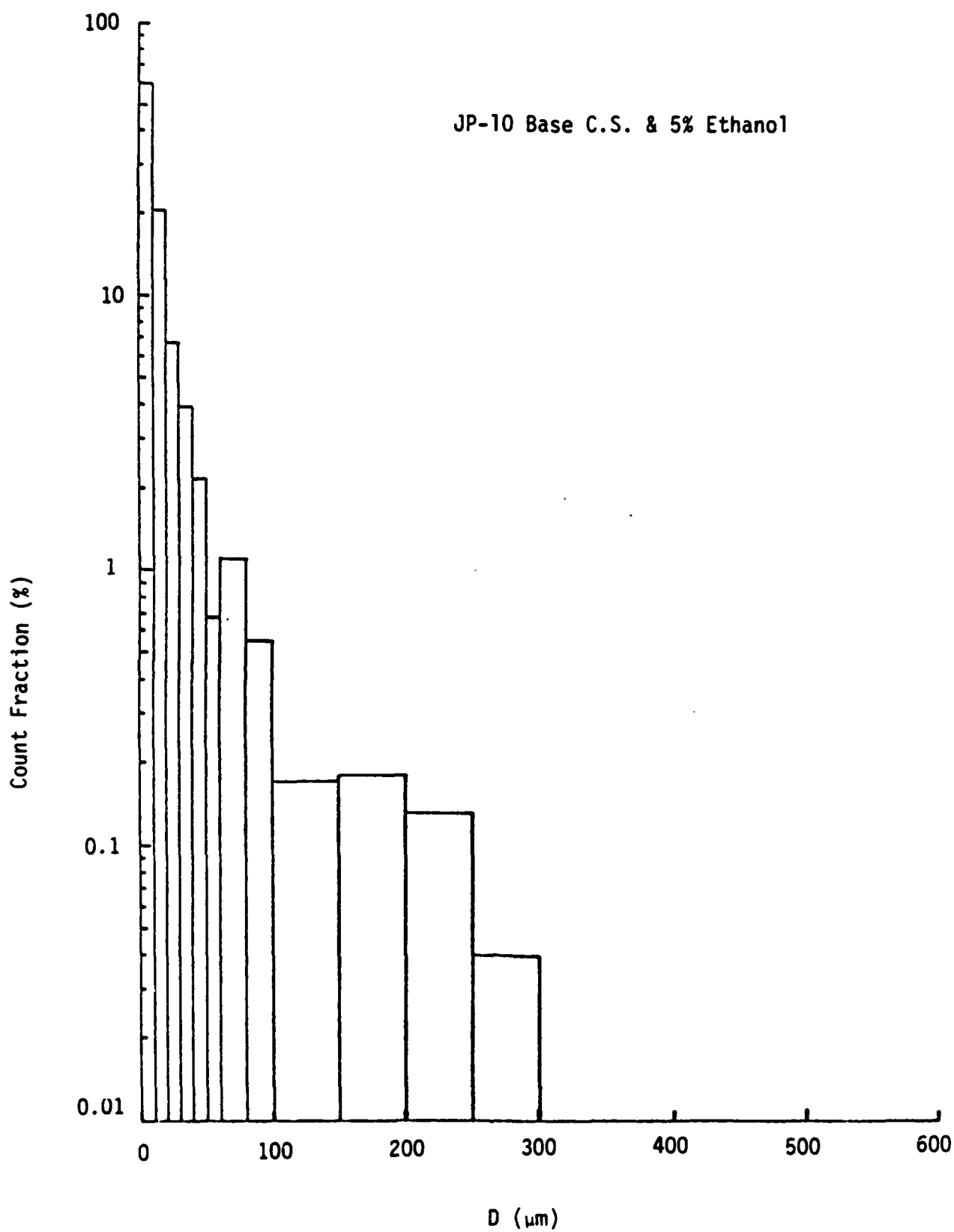
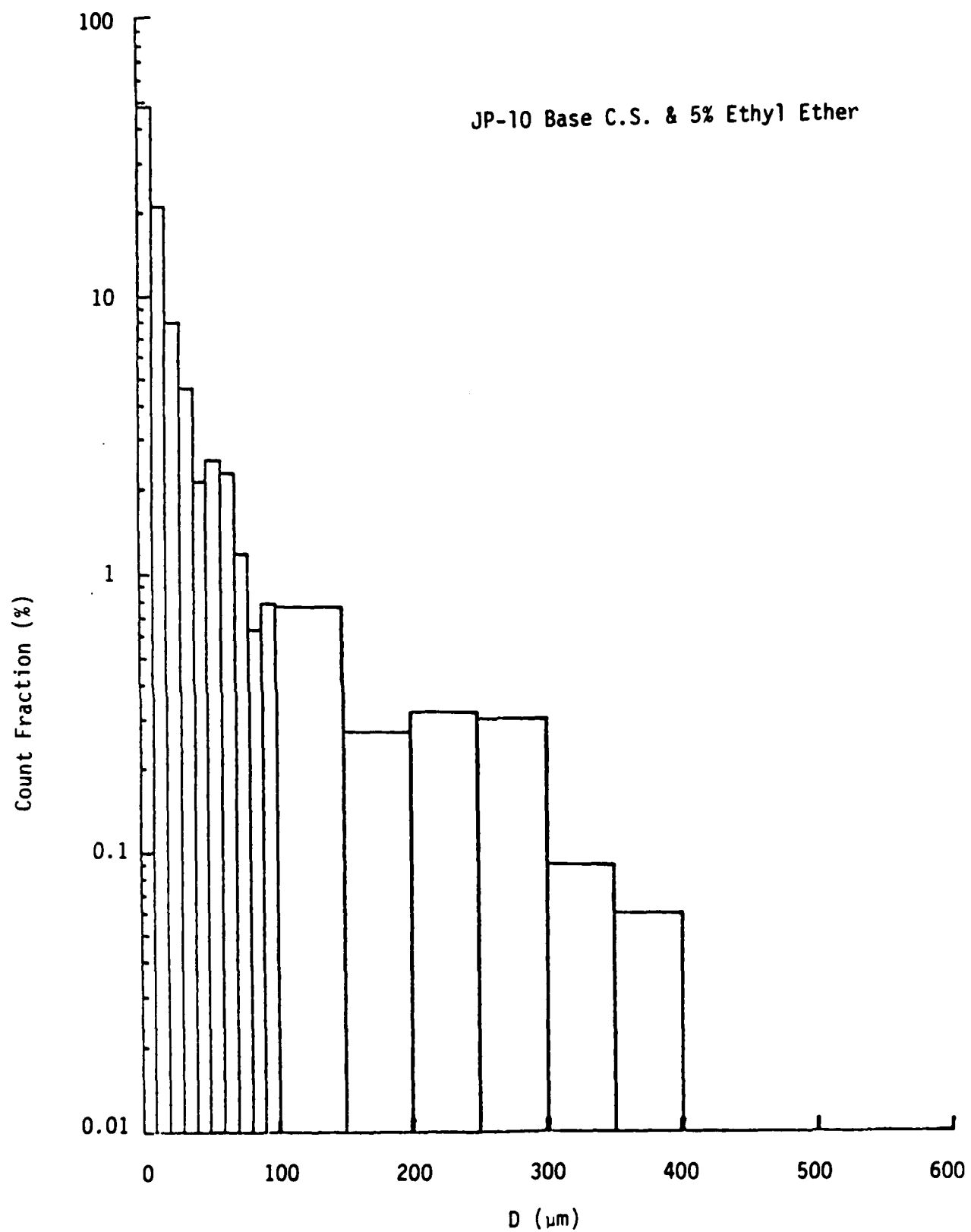FIGURE 18.   COUNT FRACTION OF EXPLODED FRAGMENTS OF CARBON SLURRY DROPLETS DOPED
WITH 5% ETHANOL

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FIGURE 19. COUNT FRACTION OF EXPLODED FRAGMENTS OF CARBON SLURRY DROPLETS WITH 5% ETHYL ETHER
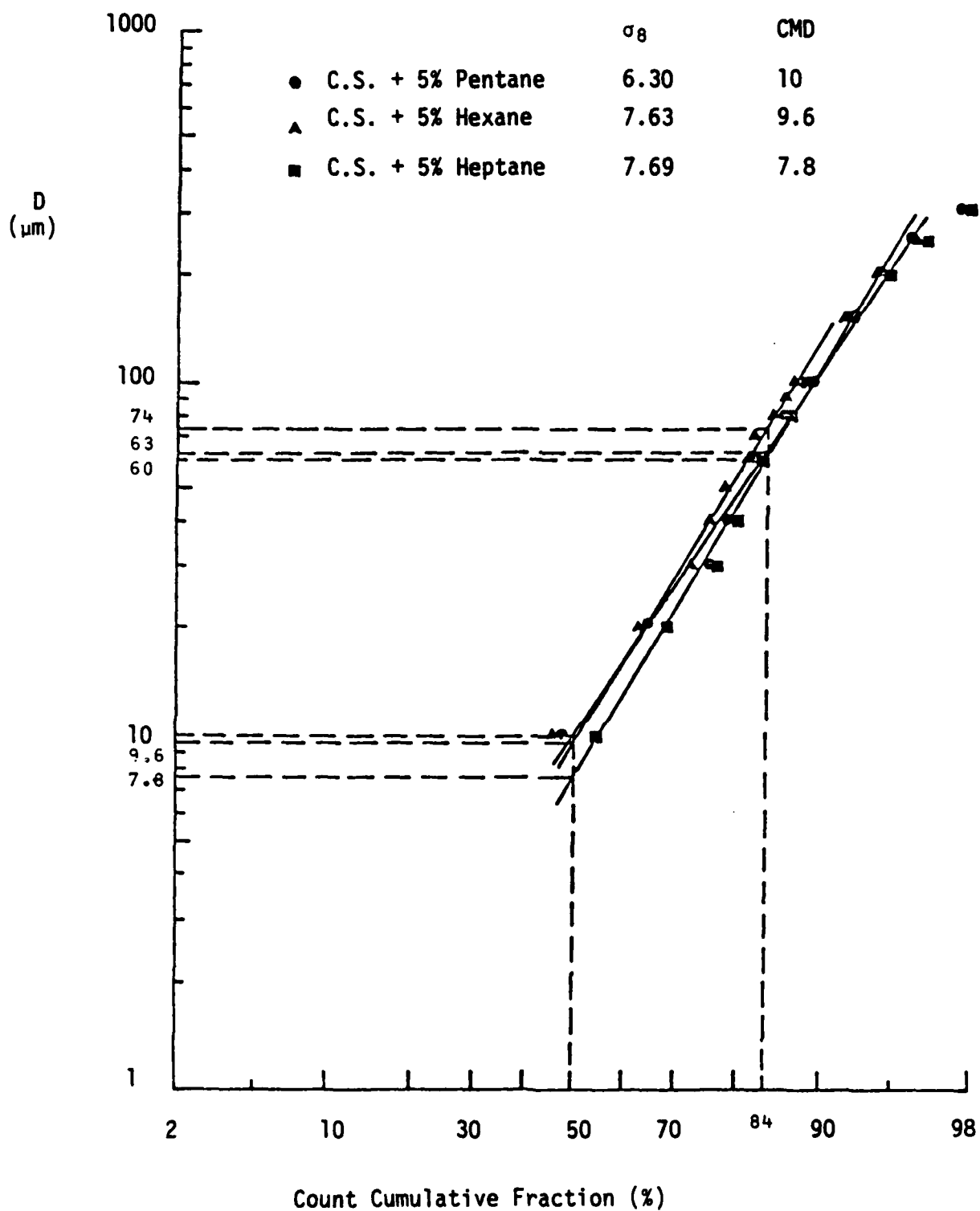
47

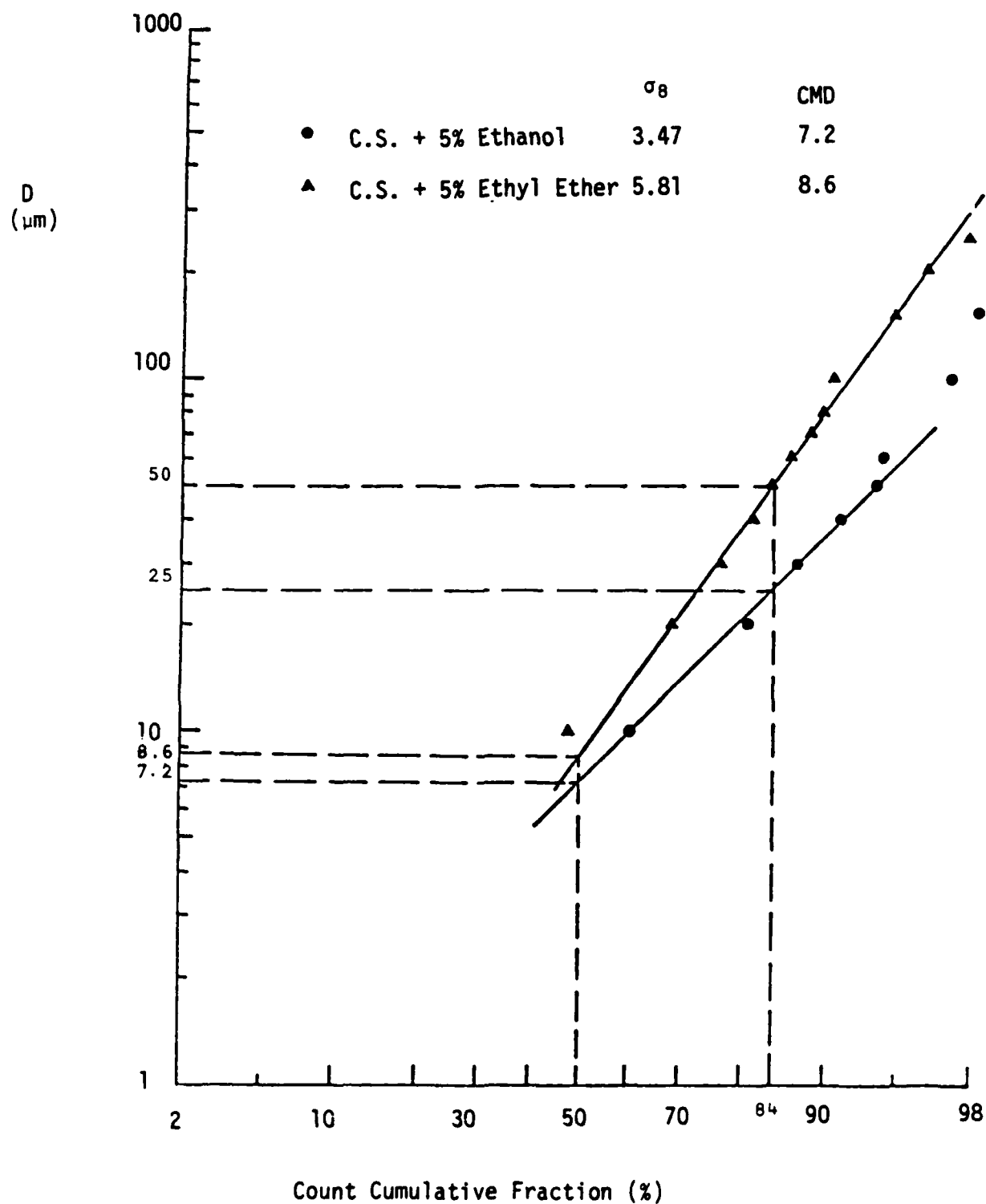FIGURE 20.   COUNT CUMULATIVE PLOT FOR CARBON SLURRY DOPED WITH PENTANE, HEXANE, AND HEPTANE .

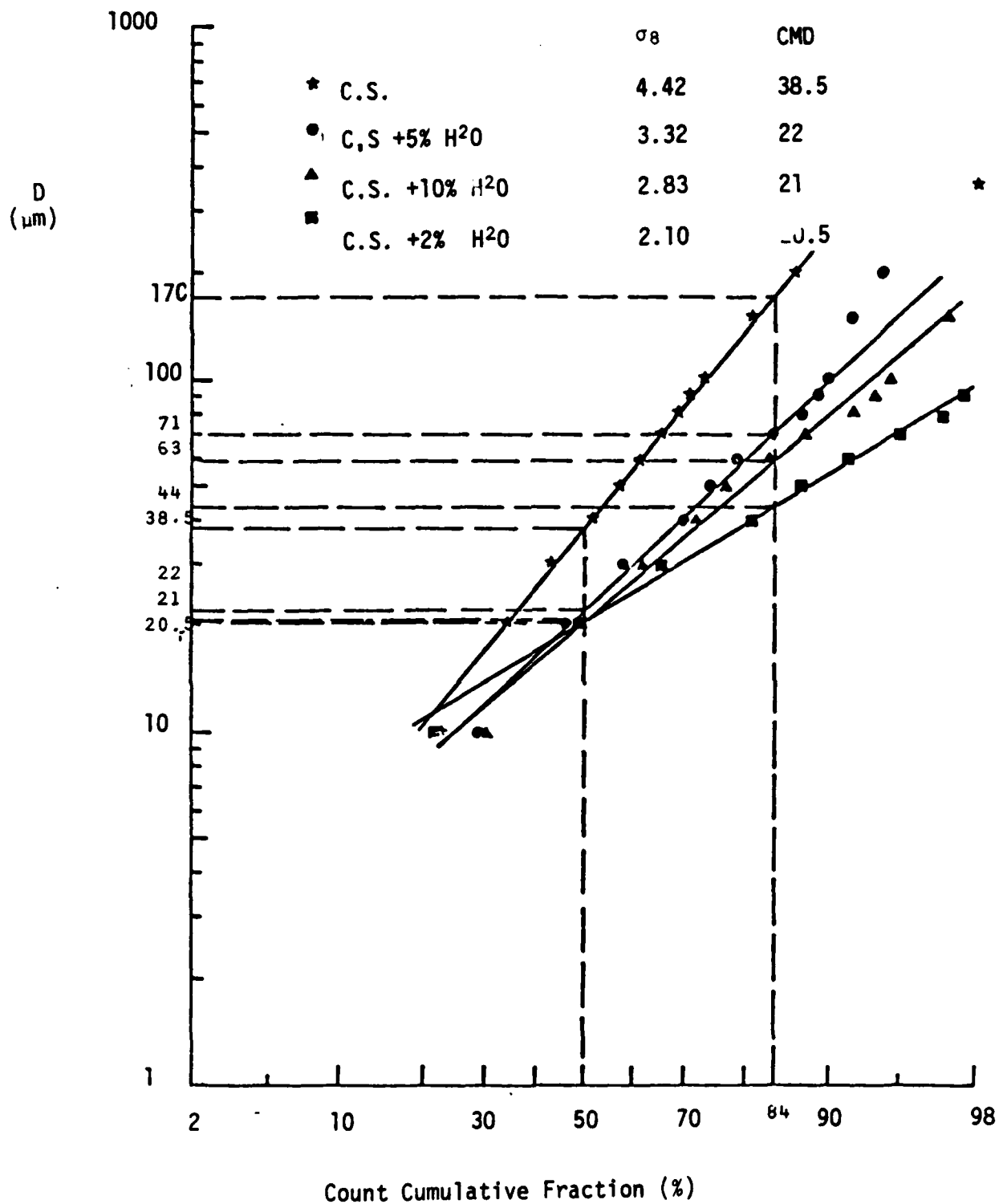FIGURE 21. COUNT CUMULATIVE PLOT FOR CARBON SLURRY DOPED WITH ETHANOL AND ETHYL ETHER

FIGURE 22.   COUNT CUMULATIVE PLOT FOR CARBON SLURRY EMULSIFIED WITH VARIOUS
             AMOUNTS OF WATER

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Recognizing the physical significance of the parameters CMD and σg, we note that carbon slurry, without additive, has a CMD of 38μm and σg = 4.42. However, in the presence of the volatile miscible additives shown in Figures 20 and 21, the CMD is reduced to values of 7 to 10μm. Furthermore, except for ethanol, the size distributions are now wider. Thus, there is definite advantage in doping the carbon slurry with small quantities (5 percent) of the volatile fuels tested herein so as to reduce the size of the agglomerate fragments.

Tests have also been run with water addition. Since water does not mix with JP-10, a 2-percent surfactant of Span 80 and Tween 85 was used for emulsification. Figure 18 shows that with water emulsification CMD is reduced, although not to the extent obtained with the volatile miscible fuels. The CMD is also not sensitive to the amount of water addition. The size distributions are narrower here.

The results with water emulsification is somewhat surprising because initially we had expected that it could be more efficient in rupturing the agglomerate. We believe that this is caused by the action of the emulsifying surfactants which have high boiling points and are very viscous. This promotes gluing of the particles, and thereby larger fragments and narrower distributions.

Finally, we note that the surfactants used in stabilizing the slurry fuel obviously also play a role in inducing microexplosion. That is, since microexplosion is not expected to occur for a mixture of only JP-10 and carbon powder, the fact that the slurry droplets do microexplode implies that their presence is essential in this phenomenon.

2. Volatile Additive Conclusions

The following conclusions can be drawn from the present study.

1. The carbon slurry fuel can microexplode without any additive, possibly due to the surfactants used for stabilization.

2. Addition of 5 percent volatile fuels, which are also miscible with the slurry fuel, can significantly reduce the average size of the agglomerate fragments. Boiling points of these additive fuels should be less than 100 C, corresponding to that of heptane.

3. Water emulsification is not as effective in rupturing the agglomerate, possibly due to the presence of the emulsifying agents used.

3. Volatile Additive Recommendations

Perform and compare some test runs with (a) existing carbon slurry and (b) existing carbon slurry doped with 5 percent heptane or any other fuel of equal or higher volatility.

V. ACKNOWLEDGMENTS

The assistance of Warren Nicholson and Dr. Harold Epstein in designing the apparatus for the CW and pulse laser experiments was much appreciated.

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